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THE POLYMORPHISM OF 4-n-PENTYLPHENYL-4′-n-BUTYLOXYTHIO-BENZOATE, (4OS5) IN THE CRYSTALLINE STATE

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The title compound, 4-n-pentylphenyl-4′-n-butyloxythiobenzoate (4OS5), $C_{22}H_{28}O_2S$, crystallized from methanol and hexane, reveals two polymorph forms in the crystalline state. The crystal and molecular structures of both polymorphs 4OS5-M (from methanol) and 4OS5-H (from hexane) are reported. 4OS5-M crystallizes in the monoclinic system, space group C2/c, with cell constants a = 39.43(2), b = 5.426(3), c = 20.392(5) Å, β = 105.15(3)°, V = 4211(3) Å^3, and Z = 8. The crystal data of 4OS5-H are: monoclinic system, space group $P2_1/c$, a=13.512(6), b=8.427(2), c=18.630(5) Å, β = 96.98(3)°, V = 2106(1) Å^3, Z = 4. The structures were solved by direct methods and refined to the final R = 0.0569 and 0.0982 for 3242 and 1498 observed reflections for 4OS5-M and 4OS5-H, respectively. The molecules of both polymorphs 4OS5 differ only in the conformation of butyloxy chain: all trans in 4OS5-M and trans-gauche-trans in 4OS5-H. Theoretical calculations made by semiempirical AM1-MNDO method showed that both conformations are stable and almost equienergetical. The unit-cell packing in crystals of 4OS5 is characterized by the occurrence of the molecular layers, additionally stabilized by the net of weak C-H…O intermolecular hydrogen bonds in 4OS5-M.

Keywords: liquid crystal; thioester; crystal and molecular structure; conformational analysis; AM1 calculations

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INTRODUCTION

In the literature there are not many papers referring to systematically structural investigations of liquid crystals. X-ray diffraction and inelastic neutron scattering studies have been carried out on derivatives of azoxybenzene, azobenzene, benzylideneaniline, cyanobiphenyl, and alkoxybenzoic acid, especially. For instance, it has been shown that there is a relationship between the mesomorphic properties and molecular structures in alkoxybenzoic acid. The nematogenic molecules crystallize in the monoclinic system [1,2] and the smectogenic ones crystallize in the triclinic system [3].

Herein we report the results of the structural studies of 4-n-pentylphenyl-4′-n-butyloxythiobenzaoate, 4OS5, belonging to an extensively investigated homologous series of the mesogenic 4-n-pentylphenyl-4′-n-alkyloxythiobenzoates, nOS5 (n varies from $n = 4$ to $n = 10$; see, for example, Chruściel et al. [4] and references therein). This compound, crystallized from methanol and hexane, reveals two polymorph forms in the crystalline state (in short 4OS5-M and 4OS5-H, respectively). The crystal and molecular structures of both polymorphs were determined by X-ray analysis and compared with previously presented crystal structures of another two compounds in the investigated series: 4-n-pentylphenyl-4′-n-pentyloxythiobenzoate, 5OS5 [5], and 4-n-pentylphenyl-4′-n-hexyloxythiobenzoate, 6OS5 [6]. The 4OS5, similarly to 5OS5, 6OS5, possesses only nematic phase during heating and cooling. Higher homologous ($n \geq F$) belonging to the series of nOS5 shows smectic polymorphism. The main goal of these studies is focused on the search for probable correlation between the structures in the crystalline state and liquid crystalline phase.

The crystallographic data of both polymorph forms of 4OS5 were used as starting models for calculating and comparing the most energetically stable conformations for isolated molecule using AM1 semiempirical method.

TABLE 1 Temperatures and Enthalpies of the Cr-N and N-I Phase Transition for the 4OS5-M and 4OS5-H

Substance	Texture of Crystalline Phase	Cr-N [°C] (kcal/mol)	N-I [°C] (kcal/mol)
4OS5-M	Fine-crystalline	62.9 (5.60)	89.7 (0.18)
4OS5-H	Lamellate	62.8 (5.65)	89.6 (0.19)

TABLE 2 Crystal Data and Structure Refinement

Data	4OS5(M)		4OS5(H)
Crystal data			
Empirical formula		$C_{22}H_{28}O_2S$	
Formula weight		356.50	
Crystal system	monoclinic		monoclinic
Space group	C2/c		$P2_1/c$
Unit cell parameters			
a(Å)	39.43(2)		13.512(6)
b(Å)	5.426(3)		8.427(2)
c(Å)	20.392(5)		18.630(5)
β	105.15(3)		96.98(3)
Volume V(Å^3)	4211(3)		2105(1)
Molecular multiplicity Z	8		4
Density (calculated; Mg/m^3)1.125		1.125	
Cell parameters from		25 reflections	
θ range for lattice parameters (°)	20.37–34.74		17.12–27.66
Absorption coefficient μ(mm^{-1})	1.439		1.439
Temperature T (K)		293(2)	
Data collection			
Collection method		$\omega/2\theta$ scans	
Absorption correction		psi scan	
T_{max}	0.999		0.995
T_{min}	0.738		0.771
θ range for data collection (°)	2.32–75.24		3.30–65.00
Index ranges			
h_{min}/h_{max}	0/48		−16/0
k_{min}/k_{max}	−6/6		−10/0
l_{min}/l_{max}	−25/24		−23/23
3 standard reflections monitored every 100 reflections			
Intensity decay (%)	−2.9		−3.7
No. of measured reflections	8093		3744
No. of independent refl. (R_{int})	4340 (0.0554)		3582 (0.0417)
No. of observed refl.	3242		1498
Refinement			
Refinement method	Full-matrix least-squares on F^2		
Final R and wR indices	0.0569, 0.2098		0.0982, 0.3553
Weight scheme	$w = 1/[\sigma^2(F_o^2)+(f_1P)^2+f_2P]$, where $P = (F_o^2+2F_c^2)/3$		
f_1, f_2	0.0991, 0.49		0.1801, 0.30
Goodness-of-fit S	1.160		1.052
Data/parameters	4269/227		3551/226
Largest diff. peak and hole (eÅ^{-3})	+0.370/−0.184		+0.296/−0.232
$(\Delta/\sigma)_{max}$	0.009		0.000

TABLE 3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Non-H Atoms with e.s.d.'s in Parentheses

Atom	x/a	y/b	z/c	U_{eq}*
4OS5(M)				
S(1)	3569(1)	926(3)	8217(1)	129(1)
O(1)	3283(1)	4512(5)	7397(1)	94(1)
O(2)	2258(1)	5162(5)	9329(1)	92(1)
C(1)	3268(1)	3356(6)	7889(2)	80(1)
C(2)	3000(1)	3794(6)	8269(2)	75(1)
C(3)	2772(1)	5770(6)	8081(2)	81(1)
C(4)	2519(1)	6287(6)	8417(2)	82(1)
C(5)	2493(1)	4816(6)	8957(2)	78(1)
C(6)	2717(1)	2830(7)	9143(2)	87(1)
C(7)	2965(1)	2320(7)	8803(2)	86(1)
C(8)	2018(1)	7175(7)	9161(2)	89(1)
C(9)	1788(1)	7162(7)	9642(2)	87(1)
C(10)	1519(1)	9208(8)	9486(2)	99(1)
C(11)	1285(1)	9236(11)	9959(3)	131(2)
C(21)	3837(1)	973(7)	7643(2)	97(1)
C(22)	4088(1)	2753(9)	7679(2)	117(1)
C(23)	4306(1)	2668(9)	7252(3)	115(1)
C(24)	4276(1)	866(7)	6775(2)	100(1)
C(25)	4017(1)	−859(8)	6733(2)	111(1)
C(26)	3801(1)	−835(8)	7160(2)	107(1)
C(27)	4517(1)	794(10)	6305(3)	128(2)
C(28)	4785(1)	−1054(11)	6452(2)	123(2)
C(29)	5032(1)	−1147(11)	6002(3)	125(2)
C(30)	5295(2)	−2938(16)	6143(4)	180(3)
C(31)	5540(2)	−3027(18)	5693(3)	185(3)
4OS5(H)				
S(1)	302(1)	2374(3)	4334(1)	145(1)
O(1)	−1245(4)	3908(6)	3732(3)	140(2)
O(2)	−3175(3)	1921(5)	6522(2)	124(2)
C(1)	−915(5)	3174(7)	4258(3)	104(2)
C(2)	−1467(4)	2838(6)	4878(3)	92(2)
C(3)	−2445(4)	3379(7)	4874(3)	101(2)
C(4)	−2978(5)	3067(7)	5412(3)	106(2)
C(5)	−2583(5)	2175(7)	6002(3)	99(2)
C(6)	−1625(5)	1608(8)	6022(3)	115(2)
C(7)	−1096(5)	1913(8)	5468(4)	111(2)
C(8)	−2780(6)	966(10)	7138(4)	154(3)
C(9)	−3544(9)	1182(17)	7706(5)	228(6)
C(10)	−4363(10)	482(17)	7507(6)	232(6)
C(11)	−5084(8)	688(16)	8153(5)	237(6)
C(21)	700(4)	2841(8)	3489(3)	104(2)
C(22)	1388(5)	4016(8)	3448(4)	118(2)
C(23)	1763(5)	4305(8)	2825(5)	126(2)
C(24)	1461(5)	3493(11)	2193(4)	122(2)
C(25)	769(6)	2306(9)	2246(4)	125(2)

(*Continued*)

TABLE 3 (Continued)

Atom	x/a	y/b	z/c	U_{eq}*
C(26)	398(5)	1989(8)	2871(5)	121(2)
C(27)	1863(7)	3920(14)	1493(4)	196(4)
C(28)	2689(8)	3327(12)	1317(5)	188(4)
C(29)	3049(8)	3646(15)	585(6)	205(5)
C(30)	3784(12)	2894(19)	338(8)	279(8)
C(31)	4023(10)	3202(16)	−369(7)	253(6)

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

EXPERIMENTAL

Crystal Data

The investigated compound has the following chemical formula:

$$H_9C_4O\text{-}C_6H_4\text{-}COS\text{-}C_6H_4\text{-}C_5H_{11}.$$

The 4OS5 sample was synthesized in the Institute of Chemistry of the University of Podlasie at Siedlce (Poland). The thioester contains two terminal groups, pentyl (-C_5H_{11}) and butyloxy (-OC_4H_9), connected to the benzene rings. Two groups in the molecule are polar: -COS- and butyloxy group.

The phase behavior, obtained by DSC using a differential scanning calorimeter (DSC type 605 M, modernized by us [7]) and polarizing microscopy (with Linkam programmable heating and cooling stage THMSE 600) methods, is shown in Table 1. The mass of samples was between 9 and 10 mg. The heating and cooling were +/−2K/min, respectively. The textures of 4OS5-M and 4OS5-H, observed by means of a polarization microscope, were fine-crystalline and lamellate, respectively. The transition temperatures and the enthalpy phase transition are comparable with experimental error (Table 1). The methanol belongs to dipole solvent groups whereas hexane belongs to nondipole groups. The influence of solvent on crystalline structure will be discussed below.

Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a methanol (4OS5-M: parallelepiped thin plates) or of a hexane (4OS5-H: rectangular thin plates) solutions. The crystals $0.80 \times 0.48 \times 0.16$ mm of 4OS5-M and $0.68 \times 0.52 \times 0.08$ mm of 4OS5-H were 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 2.

Structure Determination and Refinement

The crystal structures were solved by direct methods using SHELXS86 [8] and refined by full-matrix least squares with SHELXL93 [9]. Nonhydrogen

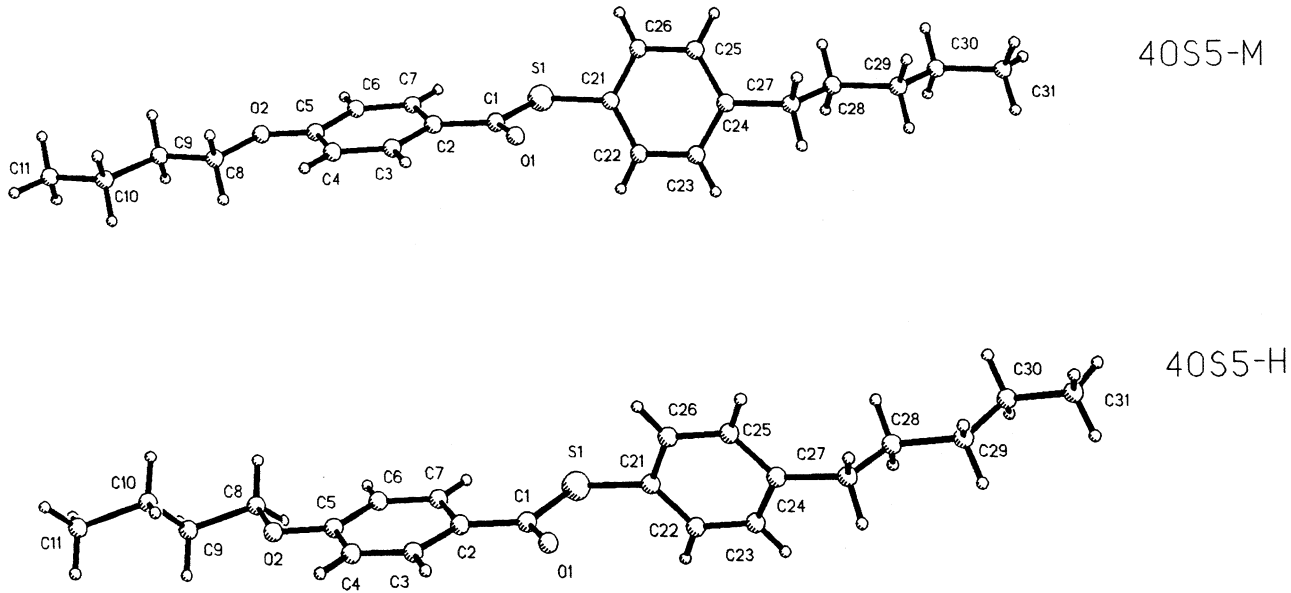

FIGURE 1 A view of the molecules 4OS5 with the atomic labelling.

TABLE 4 Bond Lengths (Å) and Angles(°) with e.s.d.'s in Parentheses

Bond Lengths and Angles	4OS5-M	4OS5-H
S(1)-C(1)	1.769(4)	1.768(7)
S(1)-C(21)	1.785(4)	1.769(6)
O(1)-C(1)	1.199(4)	1.198(6)
O(2)-C(5)	1.357(4)	1.347(7)
O(2)-C(8)	1.427(4)	1.450(7)
C(1)-C(2)	1.483(4)	1.476(8)
C(2)-C(7)	1.386(4)	1.391(8)
C(2)-C(3)	1.386(5)	1.396(7)
C(3)-C(4)	1.379(4)	1.330(7)
C(4)-C(5)	1.385(5)	1.384(8)
C(5)-C(6)	1.382(5)	1.375(8)
C(6)-C(7)	1.367(4)	1.349(8)
C(8)-C(9)	1.499(4)	1.577(13)
C(9)-C(10)	1.510(5)	1.269(11)
C(10)-C(11)	1.499(5)	1.648(13)
C(21)-C(22)	1.370(6)	1.367(8)
C(21)-C(26)	1.372(6)	1.376(9)
C(22)-C(23)	1.373(6)	1.345(8)
C(23)-C(24)	1.363(6)	1.380(9)
C(24)-C(25)	1.370(6)	1.381(10)
C(24)-C(27)	1.515(5)	1.515(10)
C(25)-C(26)	1.370(6)	1.348(9)
C(27)-C(28)	1.432(6)	1.302(10)
C(28)-C(29)	1.505(5)	1.526(11)
C(29)-C(30)	1.395(8)	1.308(14)
C(30)-C(31)	1.497(7)	1.418(14)
Angles		
C(21)-S(1)-C(1)	101.3(2)	103.0(3)
C(5)-O(2)-C(8)	118.6(2)	117.6(5)
O(1)-C(1)-C(2)	123.6(3)	124.5(6)
O(1)-C(1)-S(1)	121.7(3)	120.7(5)
C(2)-C(1)-S(1)	114.8(2)	114.7(5)
C(7)-C(2)-C(3)	118.3(3)	115.9(6)
C(7)-C(2)-C(1)	123.2(3)	123.9(6)
C(3)-C(2)-C(1)	118.5(3)	120.0(5)
C(4)-C(3)-C(2)	121.3(3)	122.0(6)
C(3)-C(4)-C(5)	119.5(3)	120.9(6)
O(2)-C(5)-C(6)	115.8(3)	124.4(6)
O(2)-C(5)-C(4)	124.7(3)	116.8(6)
C(6)-C(5)-C(4)	119.5(3)	118.8(6)
C(7)-C(6)-C(5)	120.6(3)	119.8(6)
C(6)-C(7)-C(2)	120.9(3)	122.5(6)
O(2)-C(8)-C(9)	108.4(3)	105.0(7)
C(8)-C(9)-C(10)	111.6(3)	111.7(12)
C(11)-C(10)-C(9)	112.8(4)	108.0(12)

(*Continued*)

TABLE 4 (Continued)

	4OS5-M	4OS5-H
C(26)-C(21)-C(22)	118.7(4)	117.8(6)
C(26)-C(21)-S(1)	119.8(3)	119.5(6)
C(22)-C(21)-S(1)	121.5(3)	122.5(6)
C(21)-C(22)-C(23)	120.4(4)	120.6(7)
C(24)-C(23)-C(22)	121.6(4)	122.9(7)
C(23)-C(24)-C(25)	117.4(4)	115.5(7)
C(23)-C(24)-C(27)	121.2(4)	121.1(9)
C(25)-C(24)-C(27)	121.4(4)	123.4(9)
C(26)-C(25)-C(24)	122.0(4)	122.1(7)
C(25)-C(26)-C(21)	120.0(4)	121.0(7)
C(28)-C(27)-C(24)	115.9(4)	122.3(8)
C(27)-C(28)-C(29)	117.2(4)	122.3(9)
C(30)-C(29)-C(28)	117.6(4)	124.5(11)
C(29)-C(30)-C(31)	117.4(6)	120.4(14)

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. The empirical extinction correction [9] was applied during the last few cycles of refinement of 4OS5-M: empirical isotropic extinction parameter $x = 543(88)$ with $F'_c = kF_c[1 + 0.001 \times F_c^2\lambda^3/\sin 2\theta]^{-1/4}$. Some bond lengths and angles in the side chains of 4OS5-H are deviated from the normal geometry of Csp^3-Csp^3 link. This may be explained as a disorder occurs in the somewhat larger temperature factors for peripheral atoms. The investigated compound 4OS5 has low melting point (62, 8–9°C) and the atoms in the molecule (especially peripheral atoms) have relatively large temperature factors in the room temperature. The program was supplied atomic scattering factors. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 3. Complete listing of thermal parameters and listings of observed and calculated structure factors are available from the authors on request. The molecular plots were prepared with SHELXTL-plus XP [10] and the geometrical calculations were produced using PARST [11].

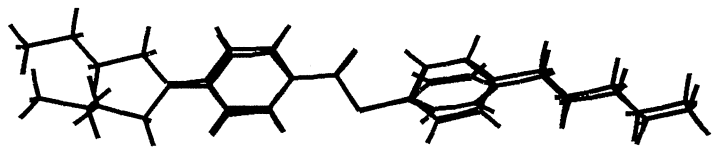

FIGURE 2 The overlay of the molecules 4OS5-M and 4OS5-H by least-squares fitting of S1, O1, C1, C2, and C21 atoms (avg. dev. of atoms 0.04(4) Å).

TABLE 5 Dihedral Angles Between the Planes

nOS5	I/II	I/III	I/IV	I/V	II/III	II/IV	II/V	III/IV	III/V	IV/V
4OS5-H	70.6	0.7	5.1	3.7	71.2	75.6	74.3	4.4	3.2	1.8
4OS5-M	102.9	—	2.5	13.8	—	103.3	95.6	—	—	12.0
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

Theoretical Calculations

The theoretical calculations were undertaken to investigate the conformational preferences of searched 4OS5 molecule. The energy minimization and geometry optimization were performed using MNDO-AM1 approximation [12] implemented in the program package HyperChem rel. 4.5 [13]. The crystallographic data of 4OS5-M and 4OS5-H were used as starting models to calculate and compare the most energetically stable conformations for isolated molecule.

RESULTS AND DISCUSSION

A view of the conformations of molecule 4OS5 was observed in both polymorph forms with numbering of the atoms is shown in Figure 1. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 3, and bond distances and valence angles in Table 4. The molecule of 4-n-pentylphenyl-4′-n-butyloxythiobenzoate, 4OS5, consists of five parts: two benzene rings C2-C7 (I) and C21-C26 (II), butyloxy chain O2-C11 (III), central part S1, O1, C1 (IV), and pentyl chain C27-C31 (V). The bond lengths, angles, and planarity of the rings in molecules 4OS5-M and 4OS5-H are very similar, and the geometry do not differ significantly from those reported for 5OS5 and 6OS5. The significant

TABLE 6 Comparison of the Torsion Angles in the Butyloxy Chain for Conformers of 4OS5-M and 4OS5-H in Crystalline State and Calculated Using AM1 Method. The Torsion Angles are: $\Psi_1 = $ C4-C5-O2-C8, $\Psi_2 = $ C5-O2-C8-C9, $\Psi_3 = $ O2-C8-C9-C10, $\Psi_4 = $ C8-C9-C10-C11

Substance	Method	Ψ_1	Ψ_2	Ψ_3	Ψ_4
4OS5-M	X-Ray	0.1	−179.9	−178.5	179.9
	AM1	−6.0	−173.2	−180.0	−178.0
4OS5-H	X-Ray	−1.0	168.9	70.9	176.8
	AM1	−6.9	−174.6	77.2	−177.1

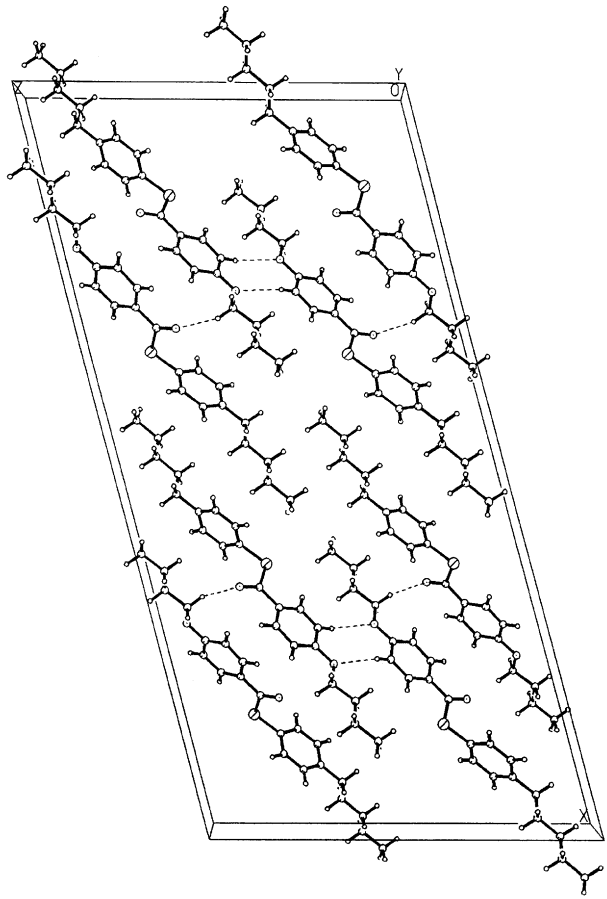

FIGURE 3 Unit-cell packing in 4OS5-M seen along the [010] direction. Broken lines indicate the hydrogen bonds.

differences occur only in the conformation of the butyloxy substituent, the torsion angles C5-O2-C8-C9—179.9(3) and 168.9(7)°, O2-C8-C9-C10—178.5(3) and 70.9(1.2)°, and C8-C9-C10-C11 179.9(4) and 176.8(7)° indicate *all trans* and *trans-gauche-trans* conformations for 4OS5-M and 4OS5-H, respectively. The overlay of both molecules in the crystalline state arranged by maximum fit at central part IV is presented in Figure 2. The mutual orientations of the main parts of both polymorph forms and the comparison of these data with those observed in 5OS5 and 6OS5 are shown in Table 5. The conformation of the molecule influences on its length, i.e., the distance between the edge H atoms. The length of 4OS5-

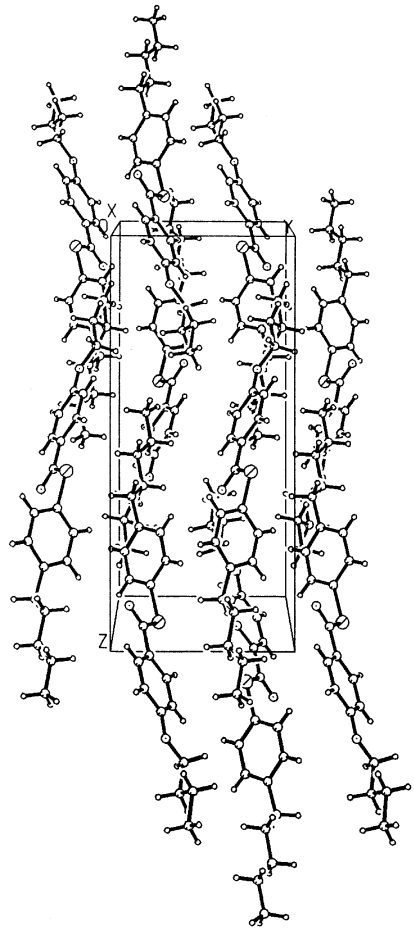

FIGURE 4 Unit-cell packing in 4OS5-H seen along the [100] direction.

M is 24.50 Å, while the length of 4OS5-H is 23.66 Å, including the covalent radii of H-atoms (0.56 Å). In comparison, the lengths of 5OS5 and 6OS5 are 25.22 and 26.25 Å, respectively.

It is worth noticing, that the *all trans* conformation for alkoxy chain, similar to that for alkyl chain, is characteristic for described molecules in the investigated homologous series nOS5. The deviation from this rule observed in one of two polymorphs of 4OS5 prompted us to further investigate the conformational preferences of this molecule using quantum-mechanics method. The initial geometries of both molecules were built from crystallographic coordinates. The starting structures were energetically

TABLE 7 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 4OS5-M

Atom	U11	U22	U33	U23	U13	U12
S(1)	129(1)	145(1)	142(1)	47(1)	90(1)	48(1)
O(1)	96(2)	107(2)	93(2)	7(1)	49(1)	−2(1)
O(2)	95(2)	105(2)	91(1)	19(1)	49(1)	21(1)
C(1)	78(2)	86(2)	83(2)	−9(2)	35(1)	−11(2)
C(2)	74(2)	83(2)	74(2)	−6(1)	29(1)	−6(1)
C(3)	86(2)	90(2)	74(2)	8(1)	33(1)	0(2)
C(4)	81(2)	88(2)	83(2)	9(2)	33(1)	10(2)
C(5)	78(2)	87(2)	75(2)	4(1)	32(1)	3(1)
C(6)	94(2)	94(2)	87(2)	18(2)	45(2)	11(2)
C(7)	89(2)	85(2)	94(2)	10(2)	43(2)	11(2)
C(8)	86(2)	97(2)	93(2)	12(2)	39(2)	14(2)
C(9)	84(2)	97(2)	89(2)	5(2)	37(2)	5(2)
C(10)	92(2)	106(3)	110(3)	−3(2)	42(2)	13(2)
C(11)	100(3)	164(5)	147(4)	−15(3)	61(3)	22(3)
C(21)	92(2)	100(2)	116(3)	16(2)	58(2)	15(2)
C(22)	115(3)	118(3)	134(3)	−32(3)	61(3)	−13(3)
C(23)	101(2)	106(3)	153(4)	−12(3)	63(3)	−19(2)
C(24)	94(2)	97(2)	125(3)	17(2)	57(2)	13(2)
C(25)	117(3)	108(3)	124(3)	−17(2)	60(2)	−7(2)
C(26)	102(2)	100(3)	136(3)	3(2)	60(2)	−10(2)
C(27)	131(3)	136(4)	146(4)	25(3)	86(3)	21(3)
C(28)	116(3)	151(4)	123(3)	28(3)	70(3)	30(3)
C(29)	116(3)	155(4)	125(3)	19(3)	68(3)	27(3)
C(30)	157(5)	218(7)	203(6)	67(6)	116(5)	69(5)
C(31)	149(5)	268(9)	169(5)	44(6)	97(4)	75(6)

minimized and geometrically optimized using AM1-MNDO method. These calculations showed that the conformations of isolated molecule of 4OS5 obtained from AM1 method do not differ significantly from those observed in the crystalline state. The comparison of calculated and experimental values of the torsion angles described the conformations of butyloxy chain, as presented in Table 6.

The AM1 calculations confirmed that the conformations of 4OS5 in crystals of both polymorph forms are energetically stable and almost equienergetical (the total energy of −5472.9 kcal/mol for 4OS5-M and −5471.7 kcal/mol for 4OS5-H). The differences in conformation of butyloxy chain (polar group) influenced the direction and value of dipole moment vector: AM1 calculated dipole moments are 1.55 and 2.40 D for 4OS5-M and 4OS5-H, respectively. In spite of differences in values of dipole moments the dipole interactions are not justified in the crystalline state in both 4OS5-M and 4OS5-H structures. The intermolecular minimum distances between sulphur—sulphur (5.426(4) Å for 4OS5-M and 4.831(4) Å

TABLE 8 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 4OS5-H

Atom	U11	U22	U33	U23	U13	U12
S(1)	110(1)	180(2)	145(2)	50(1)	14(1)	30(1)
O(1)	141(4)	154(4)	127(3)	49(3)	26(3)	43(3)
O(2)	123(3)	136(4)	115(3)	27(3)	18(3)	4(3)
C(1)	112(4)	93(4)	103(4)	4(3)	1(3)	6(3)
C(2)	108(4)	74(3)	91(4)	−5(3)	0(3)	−6(3)
C(3)	98(4)	97(4)	103(4)	13(3)	−6(3)	17(3)
C(4)	102(4)	117(5)	97(4)	13(4)	1(3)	11(4)
C(5)	103(4)	93(4)	97(4)	6(3)	2(3)	−6(3)
C(6)	119(5)	119(5)	103(4)	28(4)	1(4)	7(4)
C(7)	98(4)	110(5)	122(5)	16(4)	−2(4)	11(3)
C(8)	168(7)	173(7)	122(5)	67(5)	27(5)	3(5)
C(9)	221(11)	308(15)	146(8)	94(9)	−10(8)	−99(11)
C(10)	238(13)	255(14)	193(11)	85(10)	−16(10)	−64(11)
C(11)	208(10)	311(16)	212(10)	79(10)	104(9)	26(10)
C(21)	88(4)	105(5)	117(5)	15(4)	9(3)	16(4)
C(22)	124(5)	109(5)	123(5)	−18(4)	19(4)	−13(4)
C(23)	110(5)	123(6)	147(6)	−6(5)	20(4)	−23(4)
C(24)	105(5)	143(6)	119(6)	4(5)	16(4)	31(5)
C(25)	135(6)	114(6)	121(6)	−24(4)	−2(5)	13(5)
C(26)	127(5)	91(4)	137(6)	0(4)	−8(5)	−15(4)
C(27)	177(8)	275(12)	143(7)	27(7)	44(6)	103(8)
C(28)	184(9)	195(9)	195(9)	49(8)	62(7)	28(8)
C(29)	173(9)	266(13)	194(9)	77(9)	93(7)	46(8)
C(30)	318(20)	295(18)	246(16)	61(13)	116(15)	34(15)
C(31)	287(15)	280(16)	209(12)	−8(11)	96(11)	32(13)

for 4OS5-H) and oxygen–oxygen (5.426(3) Å, 5.759(7) Å for O1 . . . O1 and 5.426(4) Å, 7.756(7) Å for O2 . . . O2 for 4OS5-M and 4OS5-H, respectively) are more than twice the van der Waals radius ($2r_w$ of 3.70 Å for S and 2.80 for O). The missing dipole interactions in the crystalline state are characteristic for other investigated structures of compounds belonging to homologous series nOS5.

Molecular Packing

The molecular packing in the crystal of 4OS5-M is presented in Figure 3. The molecules form molecular layers are parallel to the (101) plane. Within the layer the molecules are linked by the net of very weak C-H . . . O intermolecular hydrogen bonds: C8-H81 . . . O1^{i} [C8 . . . O1 = 3.337(4), H81 . . . O1 = 2.546(4) Å, C8-H81 . . . O1 = 138.7(1)°, (i)= 1/2 − x, 1/2 + y, 1/2 − *z* + 1], C26-H261 . . . O1^{ii} [C26 . . . O1 = 3.361(5), H261 . . . O1 = 2.464(5) Å, C26-H261 . . . O1 = 161.9(1)°, (ii) = x,y−1,z] and C6-H61 . . .

TABLE 9 Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($A^2 \times 10^3$) for 4OS5-M

Hydrogen	x	y	z	U_{eq}
H(31)	2791(1)	6766(6)	7721(2)	97
H(41)	2368(1)	7614(6)	8283(2)	98
H(61)	2699(1)	1832(7)	9503(2)	105
H(71)	3112(1)	967(7)	8931(2)	103
H(81)	1875(1)	7010(7)	8697(2)	107
H(82)	2146(1)	8717(7)	9199(2)	107
H(91)	1933(1)	7351(7)	10103(2)	105
H(92)	1668(1)	5589(7)	9612(2)	105
H(101)	1640(1)	10778(8)	9515(2)	119
H(102)	1376(1)	9018(8)	9023(2)	119
H(111)	1120(1)	10564(11)	9838(3)	158
H(112)	1426(1)	9462(11)	10417(3)	158
H(113)	1161(1)	7701(11)	9925(3)	158
H(221)	4111(1)	4025(9)	7993(2)	140
H(231)	4479(1)	3870(9)	7290(3)	137
H(251)	3988(1)	−2085(8)	6404(2)	133
H(261)	3630(1)	−2044(8)	7123(2)	129
H(271)	4374(1)	541(10)	5845(3)	154
H(272)	4629(1)	2392(10)	6318(3)	154
H(281)	4672(1)	−2649(11)	6432(2)	147
H(282)	4924(1)	−815(11)	6916(2)	147
H(291)	4893(1)	−1390(11)	5538(3)	150
H(292)	5145(1)	451(11)	6020(3)	150
H(301)	5183(2)	−4537(16)	6124(4)	216
H(302)	5435(2)	−2695(16)	6606(4)	216
H(311)	5708(2)	−4327(18)	5841(3)	222
H(312)	5661(2)	−1481(18)	5717(3)	222
H(313)	5409(2)	−3329(18)	5233(3)	222

$O2^{iii}$ [C6 . . . O2 = 3.490(4), H61 . . . O2 = 2.579(4) Å, C6-H61 . . . O2 = 166.5 (1)°, (iii) = $1/2 - x$, $1/2 - y$, $-2+z$]. Similar unit-cell packing occurs in crystal of 4OS5-H (Figure 4). The molecules also form molecular layers, but these layers are parallel to the (010) plane and the intermolecular hydrogen bonds are not observed within the layer.

If, to assume, the crystal structure strongly influences on the phase situation of the substance in the mesogenic state, the molecular packing similarity in both polymorph forms of 4OS5 may determine their identity phase behavior. On the other hand, the thiobenzoates belonging to the homologous series nOS5 for n = 4, 5, 6 exhibit only nematic phase, but homologous for n > 6 show smectic polymorphism and phase behavior in the series of the investigated compounds is determined also by the length of the terminal alkoxy group. Therefore

TABLE 10 Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($A^2 \times 10^3$) for 4OS5-H

	x	y	z	U_{eq}
H(31)	−2731(4)	3976(7)	4483(3)	121
H(41)	−3626(5)	3453(7)	5391(3)	128
H(61)	−1343(5)	1017(8)	6417(3)	138
H(71)	−459(5)	1488(8)	5482(4)	134
H(81)	−2122(6)	1334(10)	7335(4)	185
H(82)	−2735(6)	−140(10)	7001(4)	185
H(91)	−3257(9)	759(17)	8169(5)	273
H(92)	−3669(9)	2304(17)	7768(5)	273
H(101)	−4245(10)	−634(17)	7422(6)	279
H(102)	−4681(10)	946(17)	7061(6)	279
H(111)	−5710(8)	165(16)	8014(5)	285
H(112)	−5199(8)	1795(16)	8231(5)	285
H(113)	−4765(8)	222(16)	8591(5)	285
H(221)	1598(5)	4622(8)	3856(4)	142
H(231)	2248(5)	5087(8)	2820(5)	151
H(251)	552(6)	1706(9)	1838(4)	150
H(261)	−69(5)	1183(8)	2884(5)	145
H(271)	1345(7)	3660(14)	1104(4)	236
H(272)	1937(7)	5065(14)	1491(4)	236
H(281)	2641(8)	2184(12)	1365(5)	226
H(282)	3218(8)	3673(12)	1683(5)	226
H(291)	2472(8)	3505(15)	226(6)	246
H(292)	3217(8)	4764(15)	581(6)	246
H(301)	3647(12)	1768(19)	366(8)	335
H(302)	4380(12)	3100(19)	671(8)	335
H(331)	4577(10)	2552(16)	−462(7)	304
H(332)	4196(10)	4301(16)	408(7)	304
H(333)	3457(10)	2962(16)	715(7)	304

the structure determination of higher homologous in the crystalline state is necessary.

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