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The Crystal and Molecular Structure of $\bar{4}$S6

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The crystal and molecular structure of 4-*n*-hexylphenyl-4′-*n*-butyloxythiolbenzoate ($\bar{4}$S6) has been determined using single crystal X-ray diffraction data. The crystals belong to the monoclinic system with space group $P2_1/c$, a = 15.726 (7) Å, b = 8.317 (4) Å, c = 17.709 (9) Å, ß = 108.25 (2)°, Z = 4. The structure of $\bar{4}$S6 has been solved by direct methods and refined to R-value of 0.0973 (R_w = 0.0725). The molecules are arranged parallel to each other and lie perpendicular to [010] alternating with $y \sim \frac{1}{4}$ and $y \sim \frac{3}{4}$ in a head-to-tail configuration. Two types of layers are discussed in the crystalline state. No dipole-dipole contacts are found.

INTRODUCTION

Crystal and molecular structures of a great number of mesogenic compounds have been determined during the last decade. Thus far no knowledge is known about a complete scheme correlating the conformation and packing of these compounds in the solid and liquid crystalline states. Therefore, further structural investigations on new mesogenic compounds should be useful.

The liquid crystalline compounds 4,4′ disubstituted phenyl thiolbenzoates were prepared and characterized by Krause *et al.*[1] and by Reynolds *et al.*[2] (1976). Recently, Haase *et al.*[3] presented thermal and X-ray structural investigations on two isomers of these compounds namely, 4-*n*-pentylphenyl-4′-cyanothiolbenzoate (NCS5) and 4-cyanophenyl-4′-*n*-pentylthiolbenzoate (5SCN). An interesting question was that concerning the molecular packing in both solid and liquid crystalline states of these isomeric compounds. Also, it is of interest to show how the different substituents affect the molecular packing and conformation of a mesogenic compound. In this respect we report here on the crystal and molecular structure of the closely related compound 4-*n*-hexylphenyl-4′-*n*-butyloxythiolbenzoate ($\bar{4}$S6).

EXPERIMENTAL

Crystal Data

The $\bar{4}$S6 sample was provided by E. Merck, Darmstadt, Germany. Suitable colorless plate-like crystals were obtained by dissolving the sample in a methanol solution and evaporating slowly at room temperature. Thermal investigations, using a differential scanning calorimeter (DSC model Du Pont 990) and texture observations by means of a polarizing microscope (Leitz Orthoplan Pol) connected with a Mettler FP82 hot stage, showed that $\bar{4}$S6 compound has the following phase behavior:

$$\text{Solid crystalline} \xrightarrow[\Delta H = 27.3 \pm 0.8 \text{ kJ/mol}]{56.9 \pm 0.2^\circ\text{C}} \text{Nematic} \xrightarrow[\Delta H = 0.8 \pm 0.2 \text{ kJ/mol}]{78.2 \pm 0.1^\circ\text{C}} \text{Isotropic liquid}$$

X-ray diffraction scans were carried at 28°C on an automatic STOE-STADI4 four-circle diffractometer with the crystal of dimensions 0.11 × 0.5 × 2.0 mm^3, mounted along [021]. The radiation used was a monochromated MoK_α (λ = 0.71069 Å). Cell parameters were determined by a least-squares refinement of 66 strong reflections within 24.6° < 2θ < 30.9°. A total of 2858 unique reflections were measured in the range 3° < 2θ < 45° (scan 2θ: ω = 1:1) of which 2294 had $F_0 < 2\sigma(F_0)$. The intensities of reflections were corrected for lorentz, polarization and absorption effects. The basic crystallographic data are summarized in Table I. X-ray diffraction measurements in the nematic phase were also carried. The experimental procedure of these measurements was reported in detail elsewhere.[4]

Structure Determination and Refinement

The structure of $\bar{4}$S6 was solved by direct methods using the program package SHELX-86.[5] The final refinement ended at R = 0.0973 (R_w = 0.0725, where $w = 0.0451/\sigma^2 (F_0)$). Anisotropic temperature factors were accounted for the non-hydrogen atoms. The difference map shows additional four peaks in the surroundings of the hexyl and butyloxy chains. Three of these peaks are adjacent to the corresponding last three carbon atoms of the hexyl group. The fourth one is adjacent to the last carbon atom of the butyloxy group. Thus, these peaks were interpreted as disordered C-atoms whose positions were weighted with 20% of a carbon atom. The coordinates of the hydrogen atoms were calculated from the idealized molecular geometry, whereby the C—H distances were fixed at 1.08 Å. In addition, the hydrogen atoms were given isotropic temperature factors fixed at 1.1 times that of the connecting carbon atoms.

Positional and anisotropic thermal parameters for the non-hydrogen atoms are listed in Table II. Lists of the observed and calculated structure factors, and the positional parameters for the hydrogen atoms are available from the authors on request.

TABLE I

Basic crystallographic data of $\bar{4}$S6

Molecular formula	$C_{23}H_{30}O_2S$
Formula weight ($g.mol^{-1}$)	370.55
Space group	$P2_1/c$
a (Å)	15.726(7)
b (Å)	8.317(4)
c (Å)	17.709(9)
ß (°)	108.25(2)
V ($Å^3$)	2199.71
Number of strong reflections used for lattice parameter refinement	66
Z	4
D_c ($g.cm^{-3}$)	1.118
F(000)	800
μ [MoK_α] (cm^{-1})	1.24
Number of reflections measured	2979
Number of independent reflections	2858
Merging R	0.0155
Number of unobserved reflections [$F_o < 2\ \sigma(F_o)$]	564
R [R_w , $w=0.0451/\sigma^2\ (F_o)$]	0.0973[0.0725]

RESULTS AND DISCUSSION

Molecular Structure

The molecular structure of $\bar{4}$S6 is presented in Figure 1 as a projection perpendicular to the phenyl ring I. It shows that the butyloxy chain is not fully extended in the gauche-conformation. The fully extended gauche-conformation is probably hindered by the rod-like packing in the crystalline state. The length of $\bar{4}$S6 molecule is 24.04 Å for the distance H(11C) . . . H(23A) including the covalent radii of the H-atoms; the crystallographic H(11C) and H(23A)-positions are: (x/a = 0.0632, y/b = 0.1934, z/c = −0.0591) and (x/a = 0.9138, y/b = 0.2321, z/c = 1.2900), respectively. The corresponding value determined from the X-ray diffraction measurements in the nematic phase is 23.8 ± 0.5Å. This leads us to presume that the

TABLE II

Positional and anisotropic thermal parameters for the non-hydrogen atoms with e.s.d.'s in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	0.5256(1)	0.2338(2)	0.5681(1)	.0814(8)	.1494(13)	.0984(10)	-.0167(9)	.0272(7)	.0223(8)
C(1)	0.4131(3)	0.3038(5)	0.5422(3)	.0781(28)	.0722(32)	.0964(35)	.0055(27)	.0363(26)	.0014(24)
O(1)	0.3845(2)	0.3684(4)	0.5896(2)	.0924(22)	.1304(29)	.0956(24)	-.0243(21)	.0307(18)	.0235(20)
C(2)	0.3591(3)	0.2714(5)	0.4584(2)	.0727(26)	.0673(29)	.0856(30)	.0037(24)	.0347(23)	.0011(22)
C(3)	0.2712(3)	0.3267(5)	0.4333(2)	.0780(27)	.0830(32)	.0839(31)	-.0059(26)	.0371(24)	.0054(25)
C(4)	0.2172(3)	0.2990(5)	0.3572(3)	.0695(26)	.0943(35)	.0933(32)	-.0076(28)	.0341(25)	.0063(25)
C(5)	0.2477(3)	0.2148(5)	0.3031(3)	.0788(28)	.0739(31)	.0887(32)	.0013(26)	.0397(25)	.0003(25)
C(6)	0.3353(3)	0.1598(5)	0.3273(3)	.0936(32)	.0878(34)	.0859(33)	-.0102(27)	.0415(27)	.0108(27)
C(7)	0.3898(3)	0.1876(5)	0.4044(3)	.0724(26)	.0837(33)	.0962(33)	-.0002(27)	.0359(26)	.0100(24)
O(2)	0.1889(2)	0.1965(4)	0.2296(2)	.0904(20)	.1125(26)	.0806(20)	-.0185(19)	.0313(17)	-.0012(18)
C(8)	0.2163(3)	0.1065(6)	0.1722(3)	.1133(36)	.1020(40)	.0967(35)	-.0221(30)	.0472(30)	.0033(31)
C(9)	0.1374(3)	0.1093(6)	0.0961(3)	.1178(39)	.1228(46)	.0900(37)	-.0231(33)	.0448(31)	-.0168(36)
C(10)	0.1163(3)	0.2718(7)	0.0603(3)	.1073(37)	.1462(53)	.0880(35)	-.0202(36)	.0220(28)	-.0112(38)
C(11)*	0.0425(3)	0.2688(7)	-0.0183(3)	.1370(20)					
C(12)	0.5657(3)	0.2791(6)	0.6710(2)	.0681(27)	.0852(34)	.0926(32)	.0041(28)	.0259(24)	.0112(26)
C(13)	0.6282(3)	0.3977(6)	0.6973(3)	.0971(34)	.0900(37)	.0974(37)	.0152(30)	.0408(29)	-.0107(30)
C(14)	0.6620(3)	0.4302(6)	0.7770(3)	.0871(31)	.0973(38)	.1060(40)	.0000(33)	.0309(30)	-.0224(28)
C(15)	0.6347(3)	0.3468(6)	0.8323(3)	.0729(27)	.0856(35)	.0937(35)	.0041(30)	.0286(26)	.0125(26)
C(16)	0.5735(3)	0.2242(6)	0.8054(3)	.0939(33)	.0859(36)	.1063(39)	.0222(30)	.0474(29)	-.0022(29)
C(17)	0.5391(3)	0.1903(5)	0.7252(3)	.0885(31)	.0813(35)	.1107(39)	-.0027(32)	.0350(30)	-.0134(26)
C(18)	0.6691(3)	0.3902(6)	0.9199(3)	.1011(35)	.1188(43)	.1000(38)	-.0017(33)	.0290(29)	.0198(33)
C(19)	0.7463(3)	0.2953(6)	0.9672(2)	.1021(33)	.0934(37)	.0993(35)	.0006(29)	.0261(28)	.0041(30)
C(20)	0.7776(3)	0.3425(6)	1.0554(3)	.1081(35)	.1252(45)	.0993(37)	-.0078(33)	.0259(29)	.0062(23)
C(21)*	0.8533(4)	0.2529(7)	1.1047(3)	.1372(20)					
C(22)*	0.8766(4)	0.3004(8)	1.1942(4)	.1768(27)					
C(23)*	0.9381(5)	0.2070(12)	1.2406(5)	.2789(47)					

* Occupation factor 0.2.

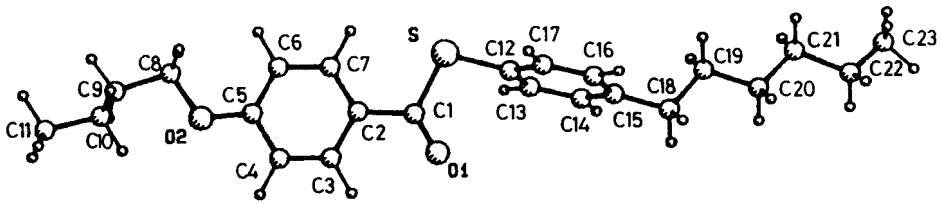

FIGURE 1 $\bar{4}$S6 molecule, projected perpendicular to the plane through the atoms C(3), C(5), and C(7) (phenyl ring I).

TABLE III

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

C(11)-C(10)	1.508(5)	C(11)-C(10)-C(9)	112.6(4)
C(10)-C(9)	1.485(6)	C(10)-C(9)-C(8)	113.9(4)
C(9)-C(8)	1.518(5)	C(9 -C(8)-O(2)	106.1(4)
C(8)-O(2)	1.435(4)	C(8)-O(2)-C(5)	118.4(3)
O(2)-C(5)	1.348(4)	O(2)-C(5)-C(4)	116.3(4)
C(5)-C(4)	1.388(5)	O(2)-C(5)-C(6)	125.1(4)
C(4)-C(3)	1.368(5)	C(4)-C(5)-C(6)	118.6(4)
C(3)-C(2)	1.391(5)	C(5)-C(4)-C(3)	121.5(4)
C(2)-C(7)	1.386(5)	C(4)-C(3)-C(2)	120.5(4)
C(7)-C(6)	1.386(5)	C(3)-C(2)-C(7)	118.1(4)
C(6)-C(5)	1.386(5)	C(3)-C(2)-C(1)	117.4(4)
C(2)-C(1)	1.485(5)	C(7)-C(2)-C(1)	124.5(4)
C(1)-O(1)	1.196(4)	C(2)-C(7)-C(6)	121.5(4)
C(1)-S	1.781(4)	C(5)-C(6)-C(7)	119.8(4)
S-C(12)	1.772(4)	C(2)-C(1)-O(1)	124.0(4)
C(12)-C(13)	1.368(5)	C(2)-C(1)-S	114.1(3)
C(13)-C(14)	1.371(5)	O(1)-C(1)-S	121.9(4)
C(14)-C(15)	1.374(5)	C(1)-S-C(12)	101.5(2)
C(15)-C(16)	1.381(6)	S-C(12)-C(13)	119.3(4)
C(16)-C(17)	1.382(5)	S-C(12)-C(17)	121.1(4)
C(17)-C(12)	1.375(5)	C(13)-C(12)-C(17)	119.5(4)
C(15)-C(18)	1.517(5)	C(12)-C(13)-C(14)	119.9(4)
C(18)-C(19)	1.470(5)	C(13)-C(14)-C(15)	121.9(4)
C(19)-C(20)	1.534(5)	C(14)-C(15)-C(16)	117.8(4)
C(20)-C(21)	1.443(6)	C(14)-C(15)-C(18)	121.2(5)
C(21)-C(22)	1.560(7)	C(16)-C(15)-C(18)	121.0(5)
C(22)-C(23)	1.311(9)	C(15)-C(16)-C(17)	120.7(4)
		C(12)-C(17)-C(16)	120.1(4)
		C(15)-C(18)-C(19)	114.9(4)
		C(18)-C(19)-C(20)	112.8(4)
		C(19)-C(20)-C(21)	115.2(4)
		C(20)-C(21)-C(22)	111.8(5)
		C(21)-C(22)-C(23)	112.3(7)

conformations of the molecules in the nematic and crystalline phases are nearly identical.

The bond distances and angles for $\bar{4}$S6 molecule are given in Table III. Whereas all the bond distances and angles in the core part of the molecule (C(5) to C(15)) are found to be of normal order of magnitudes, as compared with their corre-

TABLE IV

Dihedral angles between best planes defined in Figure 1

Planes	I/II	I/III	I/IV	I/V	II/III	II/IV	II/V	III/IV	III/V	IV/V
Angle(°)	-74.2	30.0	3.5	22.4	76.6	-71.8	84.8	31.9	8.2	23.9

sponding values for NCS5[3] and 5SCN[6], some of them in the hexyl group (C(20)–C(21), C(21)–C(22) and C(22)–C(23)) are anomalous (Table III). This is resulting from the disordering of some C-atoms in this group (Table II). The dihedral angles between the best planes formed through the subunits of the $\bar{4}$S6 molecule (Figure 1) are given in Table IV. An interesting point of consideration is the dihedral angle between the best planes through the phenyl groups which differs in sign (−74.2°) with respect to its corresponding (69.0°) for NCS5.[3] We interpret this difference in terms of the different packing in the crystalline state of each compound. Table IV shows that the thiolbenzoate group (I/IV) is virtually coplanar similar to that for NCS5.[3]

Molecular Packing

The packing of $\bar{4}$S6 molecules in the crystalline state is shown in Figure 2. It is arranged in such a manner that the molecules are extended parallel to each other and lie perpendicular to [010] alternating with $y \sim \frac{1}{4}$ and $y \sim \frac{3}{4}$ in a head-to-tail

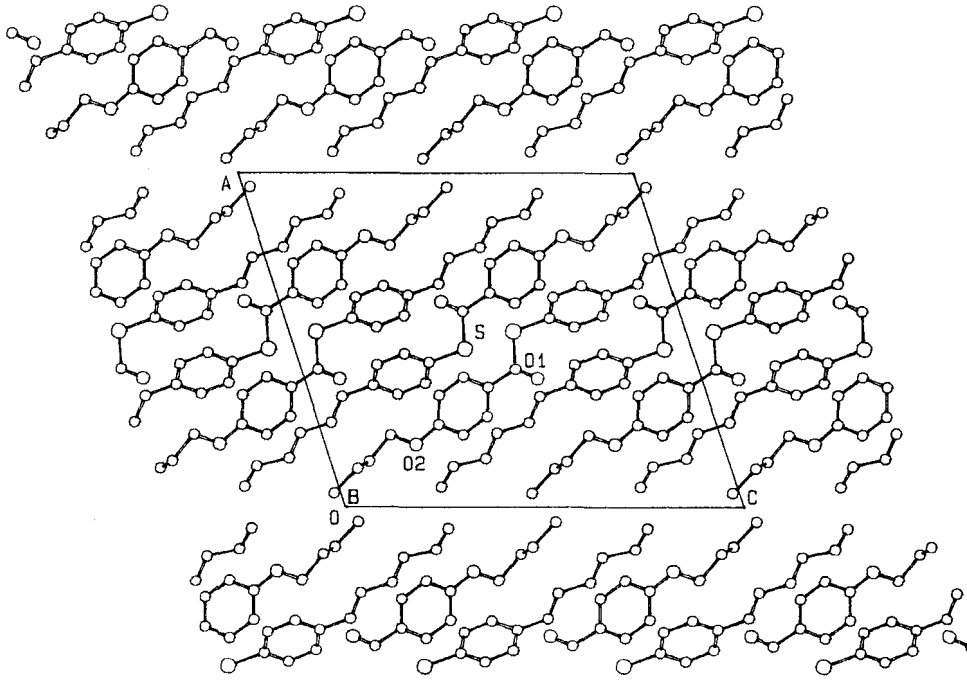

FIGURE 2 An orthogonal projection of the unit cell contents along the [010].

configuration. The projection of the long molecular axis on the (010) plane makes an angle of ~33° with the *c*-axis.

There are two types of layers; the first of which lies parallel to [001] alternating with y, $\bar{y}$, $\frac{1}{2} + y$ and $\frac{1}{2} - y$. The second type is perpendicular to [100] and has a thickness of half of the crystallographic *a*-axis (=7.86 Å).

Dipole-dipole contacts are not justified by any of the calculated intermolecular distances between the non-hydrogen atoms. The sulphur-sulphur distance across the crystallographic center is ~4.51 Å, which is much greater than twice the van der Waals radius of sulphur (1.85 Å) as compared with the corresponding value for NCS5[3] (3.85 Å).

In conclusion, these measurements support the idea that there is a simple structural correlation between the solid crystalline and nematic phases. Evidently the 2_1-related molecules are responsible for the formation of the nematic phase at the solid crystalline-nematic phase transition. This can be confirmed by the results obtained for liquid crystalline compounds whose structures are known.[7-14]

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