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Structural studies of some *o*-substituted *S*-phenyl thiobenzoates. I. Crystal structure of *S*-phenyl *o*-chlorothiobenzoate and *S*-phenyl *o*-bromothiobenzoate

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Structural characteristics of *S*-phenyl *o*-chlorothiobenzoate (**I**) and *S*-phenyl *o*-bromothiobenzoate (**II**) have been investigated by single crystal X-ray diffraction. It was shown that the crystals are isomorphous and crystallize in the monoclinic space group $P2_1$ with $Z = 2$. The unit cell parameters are: $a = 10.150(3)$, $b = 7.672(2)$, $c = 7.595(2)$ Å, $\beta = 91.28(1)°$ for $C_{13}H_9ClOS$ (compound **I**) and $a = 10.141(3)$, $b = 7.764(2)$, $c = 7.653(2)$ Å, $\beta = 90.14(3)°$ for $C_{13}H_9BrOS$ (compound **II**). The structures were solved by heavy-atom methods and refined by full-matrix least-squares, from room-temperature data collected with a Philips PW 1100 diffractometer, to conventional R factors of 0.056 for **I** and 0.044 for **II**. The structures consist of independent molecules held together by intermolecular interactions. Molecular packing is influenced by the presence of *o*-substituted Cl or Br atoms. The Cl atoms in structure **I** as well as the Br ones in structure **II** are directed to the centers of the pi-electronic system of the *o*-substituted phenyl rings belonging to the neighboring molecules. The six Cl · · · C and Br · · · C distances range from 3.651(10) to 3.869(9) Å and from 3.644(6) to 3.890(6) Å, respectively. The Cl (or Br) atom is additionally directed towards the two carbon atoms (C3 and C4) in another *o*-substituted phenyl ring, the Cl · · · C and Br · · · C distances being 3.786(9) and 3.849(10) Å in **I** and 3.727(6) and 3.881(6) Å in **II**. The torsion angle C6—C7—S—C8 is −170.2(7)° in **I** and 168.6(4)° in **II**. The angles between the planar O—C7—S central fragment of the molecule, on the one hand, and the *o*-substituted phenyl ring, on the other, are 113.9(3)° in **I** and 110.9(2)° in **II**. The corresponding values for the angles between the O—C7—S fragment and the nonsubstituted phenyl ring are 115.8(3)° and 114.3(2)° in compounds **I** and **II**, respectively.

Introduction

The structural characteristics of *o*-substituted *S*-phenyl thiobenzoates dissolved in different solvents have been studied using various techniques: infrared spectroscopy (Nyquist and Potts, 1959; Prangova *et al.*, 1987); polarographic methods (Prangova *et al.*, 1985); and dipole moment measurements (Prangova *et al.*, 1987). Very few data about the IR spectra in the solid state (KBr pellets) have been reported (Prangova *et al.*, 1985). To the best of our knowledge, there are no reports about the crystal structure determinations of *o*-substituted *S*-phenyl thiobenzoates. We have undertaken a systematic study of the structural properties of *o*-substituted *S*-phenyl thiobenzoates in the solid state using single crystal X-ray diffraction and infrared spectroscopy. Presently reported are the results of the crystal structure determination of the isomorphous *o*-Cl and *o*-Br *S*-phenyl thiobenzoates.

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Experimental

Both compounds, *S*-phenyl *o*-chlorothiobenzoate (**I**) and *S*-phenyl *o*-bromothiobenzoate (**II**) were prepared according to Prangova *et al.*, (1985) by mixing of equimolar quantities of pyridine solution of thiophenol and corresponding *o*-substituted benzoyl chloride in the presence of nitrogen. Found: C, 63.07; H, 3.83% for **I** and C, 53.36; H, 3.22% for **II**. Calculated: C, 62.68; H, 3.62% for **I** ($C_{13}H_9ClOS$) and C, 53.24; H, 3.07% for **II** ($C_{13}H_9BrOS$). The single crystals (transparent prisms) for data collection were grown from ethanolic solution.

Information concerning crystal data, parameters for data collection and refinement conditions are shown in Table 1.

The data for the accurate determination of cell parameters by a least-squares analysis of the setting angles (14 reflections in the range $7° < \theta < 12°$ for **I** and 16 reflections in the range $8° < \theta < 10°$ for **II**) and intensity data were collected at room temperature on a Philips PW 1100 automatic four-circle diffractom-

Table 1. Crystal data, data collection, and refinement conditions

	Compound (**I**)	Compound (**II**)
Crystal data		
Formula	$C_{13}H_9ClOS$	$C_{13}H_9BrOS$
M_r	248.73	293.18
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a/Å	10.150(3)	10.141(3)
b/Å	7.672(2)	7.764(2)
c/Å	7.595(2)	7.653(2)
β/°	91.28(1)	90.14(3)
V/Å^3	591.3(3)	602.6(3)
Z	2	2
D_x/(g cm^{-3})	1.40	1.62
λ(Mo $K\alpha$)/Å	0.7107	0.7107
μ(Mo $K\alpha$)/cm^{-1}	4.64	35.18
F(000)	256	292
Data collection		
Crystal size/mm	0.15 × 0.11 × 0.09	0.50 × 0.21 × 0.15
Scan mode	$\theta - 2\theta$	$\theta - 2\theta$
θ range/°	$2 < \theta < 27$	$2 < \theta < 28$
Scan speed/(° s^{-1})	0.05	0.06
Scan width/°	1.50	1.40
Number of reflections measured	1309	3638
Number of unique reflections	1222	2289
R_{int}	0.012	0.058
Number of reflections used in the refinement [$I \geq 3\sigma(I)$]	1058	1864
Index range		
h	−11 to 12	−13 to 13
k	−9 to 9	−10 to 10
l	0 to 9	−10 to 10
Refinement		
Number of parameters refined	144	144
k in weighting scheme $w = 1/[\sigma^2(F_o) + k(F_o)^2]$	0.0024	0.0012
Max and min electron density in the last ΔF map/(e Å^{-3})	0.30; −0.32	0.45; −0.57
$(\Delta/\sigma)_{max}$	0.004	0.005
Final R	0.056	0.044
Final wR	0.075	0.055

eter, graphite-monochromated Mo $K\alpha$ radiation. The intensities of three reflections measured every 2 hr showed no evidence of crystal decay. The data were corrected for Lorentz and polarization factors but not for absorption effects.

The structures were solved by means of Fourier synthesis based upon the Br-atom coordinates (in **II**) obtained from the Patterson map. The positions of all nonhydrogen atoms were found by the heavy-atom method. Both structures were refined (on F) by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters (for the non-hydrogen atoms). The difference Fourier map showed maxima in positions consistent with the expected locations of the H atoms. In the final rounds of calculations, the H atoms were positioned on geometrical grounds (C—H 0.95 Å) and included (as riding atoms) in the structure-factor calculations but not refined. The isotropic thermal parameters of the hydrogen atoms were calculated from the value of the bonded carbon atoms anisotropic thermal parameters. The final least-squares refinement including 144 variable parameters resulted in a final R of 0.056 for **I** and 0.044 for **II** [opposite hand: $R = 0.057$ (**I**), $R = 0.054$ (**II**)]. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed using a Univac 1110 computer of the Zagreb University Computing Center, SRCE and on a personal computer (microprocessor 80386/25 MHz and mathematical coprocessor 80387) using SHELX76 (Sheldrick, 1976) and NRCVAX (Gabe *et al.*, 1989). The ORTEPII program (Johnson, 1976) was used to generate the illustrations.

Table 2. Final atomic coordinates ($\times 10^4$, $\times 10^5$ for Br) and equivalent isotropic thermal parameters B_{eq} (Å^2) for (**I**) and (**II**)

	x	y	z	B_{eq}[a]
(**I**)				
Cl	9403(3)	0	6365(4)	6.7(2)
S	5440(2)	−861(5)	5034(3)	4.1(1)
O	7168(6)	−2936(11)	6597(9)	4.8(3)
C1	9026(8)	−752(13)	4232(11)	3.6(4)
C2	9897(8)	−382(13)	2924(12)	4.2(5)
C3	9581(8)	−892(16)	1267(11)	4.1(4)
C4	8448(10)	−1843(14)	874(12)	4.3(5)
C5	7602(8)	−2176(12)	2205(11)	3.6(4)
C6	7876(7)	−1651(11)	3895(11)	2.7(4)
C7	6941(8)	−2034(11)	5396(11)	2.8(4)
C8	4622(8)	−1155(12)	7053(11)	3.1(4)
C9	3371(9)	−1900(13)	7034(13)	4.3(5)
C10	2700(9)	−1977(14)	8607(15)	4.9(6)
C11	3256(12)	−1349(14)	10123(14)	5.0(5)
C12	4476(10)	−558(16)	10138(11)	4.8(5)
C13	5136(8)	−476(12)	8534(13)	3.7(4)
(**II**)				
Br	6473(8)	0	36335(8)	6.45(4)
S	4585(1)	1070(2)	4969(2)	4.08(6)
O	2856(4)	3157(6)	3479(5)	4.5(2)
C1	1036(5)	883(7)	5875(7)	3.3(2)
C2	175(5)	511(7)	7240(8)	4.0(2)
C3	464(6)	1114(10)	8902(8)	4.6(3)
C4	1573(6)	2071(8)	9186(7)	4.1(2)
C5	2440(5)	2414(8)	7863(7)	3.6(2)
C6	2158(5)	1831(6)	6161(6)	2.9(2)
C7	3096(4)	2231(7)	4676(6)	2.9(2)
C8	5387(5)	1355(7)	2929(7)	3.1(2)
C9	6593(5)	2108(8)	2855(8)	4.2(2)
C10	7259(6)	2205(9)	1265(11)	5.3(3)
C11	6733(7)	1513(9)	−197(9)	4.9(3)
C12	5514(6)	761(10)	−123(8)	4.9(3)
C13	4827(5)	665(8)	1433(7)	4.0(3)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Results and discussion

The final fractional atomic coordinates and values of the bond distances and bond angles for compounds **I** and **II** are given in Tables 2 and 3, respectively.[4] Since the structures are isomorphous, we present only the illustrations for the Br-derivative. Two different views of the molecule including the atom-labeling scheme are shown in Fig. 1 whereas the packing of the molecules in the unit cell is presented in Fig. 2. The direction of the Br atom towards the pi-electronic system of the *o*-substituted phenyl ring of the neighboring molecule is illustrated in Fig. 3.

Both structures consist of independent $C_{13}H_9ClOS$ or $C_{13}H_9BrOS$ molecules (see Fig. 2). As expected, the packing of the molecules in the unit cell is influenced by the presence of the *o*-substituted Cl or Br atoms.

The most interesting feature in the two isomorphous structures is the fact that the chlorine atoms (in structure **I**) and the bromine atoms (in structure **II**) point toward the centers of the pi-electronic system of the *o*-substituted phenyl rings belonging to the neighboring molecules (Isaacs, 1972; Mulliken, 1952; Dewar and Lepley, 1961) (see Fig. 3). The Cl · · · C distances in **I** and Br · · · C distances in **II** are very close to each other and range from 3.651(10) to 3.869(9) Å for **I** and from

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[4] The tables of anisotropic thermal parameters, torsion angles, calculated hydrogen coordinates, least-squares planes and observed and calculated structure factors are deposited with the Journal and available from the Editor on request.

Table 3. Bond lengths (Å) and angles (°) for (**I**) and (**II**)

	(**I**)	(**II**)
Br—C1	—	1.888(5)
Cl—C1	1.754(9)	—
S—C7	1.786(9)	1.772(5)
S—C8	1.774(8)	1.776(5)
O—C7	1.164(12)	1.190(6)
C1—C2	1.374(11)	1.393(7)
C1—C6	1.375(11)	1.372(7)
C2—C3	1.350(13)	1.386(9)
C3—C4	1.388(15)	1.365(9)
C4—C5	1.365(13)	1.369(8)
C5—C6	1.368(12)	1.408(7)
C6—C7	1.528(12)	1.516(7)
C8—C9	1.392(12)	1.356(7)
C8—C13	1.336(13)	1.385(8)
C9—C10	1.389(14)	1.395(9)
C10—C11	1.358(17)	1.350(12)
C11—C12	1.379(17)	1.368(11)
C12—C13	1.405(13)	1.383(8)
C7—S—C8	102.5(4)	102.6(2)
Br—C1—C2	—	118.4(4)
Cl—C1—C2	118.0(7)	—
Br—C1—C6	—	120.7(4)
Cl—C1—C6	120.2(6)	120.7(4)
C2—C1—C6	121.7(8)	120.8(5)
C1—C2—C3	118.1(8)	119.1(5)
C2—C3—C4	122.1(7)	120.1(5)
C3—C4—C5	118.1(8)	121.2(5)
C4—C5—C6	121.5(8)	119.5(5)
C1—C6—C5	118.4(7)	119.1(5)
C1—C6—C7	119.8(7)	120.8(4)
C5—C6—C7	121.8(7)	120.1(4)
S—C7—O	125.0(7)	125.3(4)
S—C7—C6	109.3(6)	109.7(3)
O—C7—C6	125.7(8)	125.0(4)
S—C8—C9	119.2(7)	120.4(4)
S—C8—C13	119.8(7)	119.4(4)
C9—C8—C13	120.5(8)	120.0(5)
C8—C9—C10	118.2(9)	119.9(6)
C9—C10—C11	120.7(9)	120.6(6)
C10—C11—C12	121.3(9)	119.4(6)
C11—C12—C13	117.3(9)	121.0(6)
C8—C13—C12	121.9(8)	119.0(5)

3.644(6)to 3.890(6) Å for **II**. At the same time, the Cl atom in **I** and the Br atom in **II** are additionally directed toward two carbon atoms (C3 and C4) from another *o*-substituted phenyl ring of the title molecule (see Fig. 3), the Cl · · · C and Br · · · C distances being 3.786(9) and 3.849(10) Å in **I** and 3.727(6) and 3.881(6) Å in **II**.

The torsion angle C6—C7—S—C8 is −170.2(7)° in **I** and 168.6(4)° in **II**. These values are not in a com-

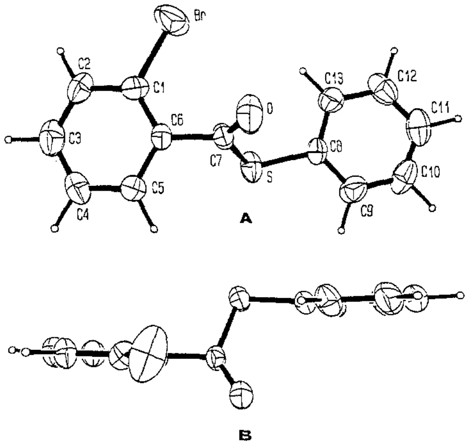

Fig. 1. An ORTEPII (Johnson, 1976) drawing of the bromine derivative (**II**) showing the crystallographic numbering scheme. View perpendicular to the benzene rings plane (A). Upper orientation rotated 90° around C6—C7 bond (B). Thermal ellipsoids at 50% probability level. H atoms are represented by circles of arbitrary radius.

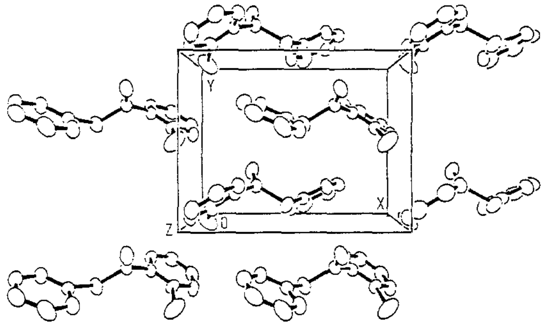

Fig. 2. Packing of the molecules of bromine derivative (**II**) in the unit cell (Johnson, 1976).

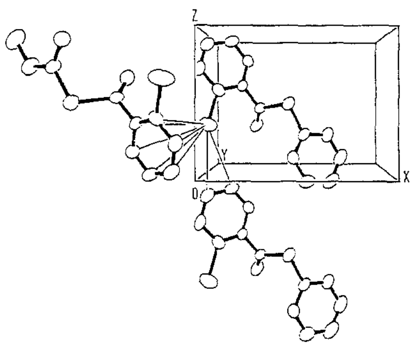

Fig. 3. Packing diagram of bromine derivative (**II**) showing the approaching of the bromine atom to the benzene ring of adjacent molecules.

plete agreement with the results based on the dipole moment measurements of the two compounds in the solution of CCl_4 and $CHCl_3$ (Prangova *et al.*, 1987). Namely, Prangova and co-workers have concluded that the *S*-phenyl bond lies in the plane of the C=O bond. The angle between the planar O—C7—S fragment of the molecule, on the other hand, and the *o*-substituted phenyl ring, on the other, is 113.9(3)° in **I** and 110.9(2)° in **II.** The values for the angles between the O—C7—S fragment and the nonsubstituted phenyl ring are 115.8(3)° and 114.3(2)° for **I** and **II,** respectively.

The two terminal phenyl rings of the molecule are almost parallel to each other, being only slightly twisted [by an angle of 3.8(3)° in **I** and 4.7(2)° in **II;** see Fig. 1]. The *o*-substituted Cl (or Br) atom is closer to the neighboring *O* atom [the corresponding distances are 3.205(8) Å and 3.323(4) Å, for **I** and **II**] than to the *S* atom [4.178(4) Å and 4.203(1) Å, respectively], but still far from being in a *cis* position as has been indicated on the basis of the infrared investigation of the same compounds in solution (Nyquist and Potts, 1959). Otherwise, the distance of the Cl atom in **I** and that of the Br atom in **II** from the least-squares plane of the *o*-substituted phenyl ring are 0.042(14) and 0.044(8) Å, respectively.

There are no significant differences between the C—C distances and C—C—C angles in the *o*-substituted phenyl ring, on the one hand, and in the phenyl ring bound to sulfur, on the other (see Table 3). The Cl—Cl and Cl—Br bonds of 1.754(9) and 1.888(5) Å, respectively, the C7=O distances [1.164(12) Å in **I** and 1.190(6) Å in **II**] and the S—C8 bond lengths [1.774(8) Å in **I** and 1.776(5) Å in **II**] are close to the corresponding values found in similar structures with C—Cl, C—Br, C=O and S—C bonds (e.g., Ohrt and Parthasarathy, 1972; Gougoutas and Lessinger, 1973; Kato, 1972).

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Thermal parameter, torsion angles, H atom coordinates, least squares planes and structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication no. 63223 (25 pages).