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ORIGINAL PAPER

Synthesis and Crystal Structures of Diaryl Thioethers and Aryl Benzyl Thioethers Derived from Thiosalicylic Acid

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Abstract

Reaction of thiosalicylic acid and iodobenzene or 1-fluoro-2-nitrobenzene in the presence of two equiv. of K_2CO_3 in acetone–water afforded the according diaryl thioethers **1** and **2** bearing carboxyl groups. Treatment of thiosalicylic acid with benzyl bromide-type compounds under similar reaction conditions gave aryl benzyl thioethers **3**–**8** in excellent yields. Moreover, reactions of thiosalicylic acid and benzyl bromide in the presence of excess K_2CO_3 led to isolation of compound **9** (Leka et al. in Acta Cryst E69:o285–0286, 2013) through further esterification of the carboxyl group. Crystal structures of **2, 5–7** and **9** (Leka et al. in Acta Cryst E69:o285–0286, 2013), along with their spectroscopic properties are reported. Weak hydrogen-bonding interactions exist in compound **2** and isomers **5**–**7**. Compounds **2** and **7** crystallize in the monoclinic space group $P2_1/n$ and $C2/c$, respectively, with $a = 12.04(3)$, $b = 7.311(19)$, $C = 14.22(4)$ Å, $\beta = 93.94(3)°$, and $Z = 4$ for **2**, and $a = 14.934(13)$, $b = 5.116(5)$, $C = 33.76(3)$ Å, $\beta = 91.523(12)°$, and $Z = 8$ for **7**. The unit cell of **5** has triclinic P-1 symmetry with the cell parameters $a = 5.4334(14)$, $b = 7.7787(19)$, $C = 16.488(4)$ Å, $\alpha = 76.601(3)°$, $\beta = 86.078(3)°$, $\gamma = 70.772(3)°$, and $Z = 2$ for **5**. Compound **6** crystallizes in the orthorhombic space group $Pbca$ with $a = 15.1881(12)$, $b = 7.3288(6)$, $C = 23.7366(19)$ Å, and $Z = 8$.

Graphical Abstract

Reactions of thiosalicylic acid and a series of aryl- or benzyl halides in the presence of K_2CO_3 in acetone–water resulted in the formation of according diaryl thioethers and aryl benzyl thioethers in excellent yields.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10870-018-0705-7) contains supplementary material, which is available to authorized users.

Extended author information available on the last page of the article

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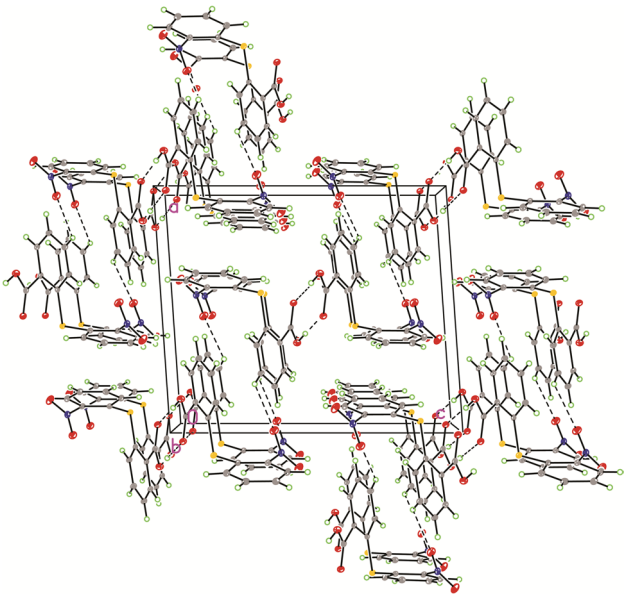


Keywords Thiosalicylic acid · Aryl sulfide · Synthesis · X-ray structure

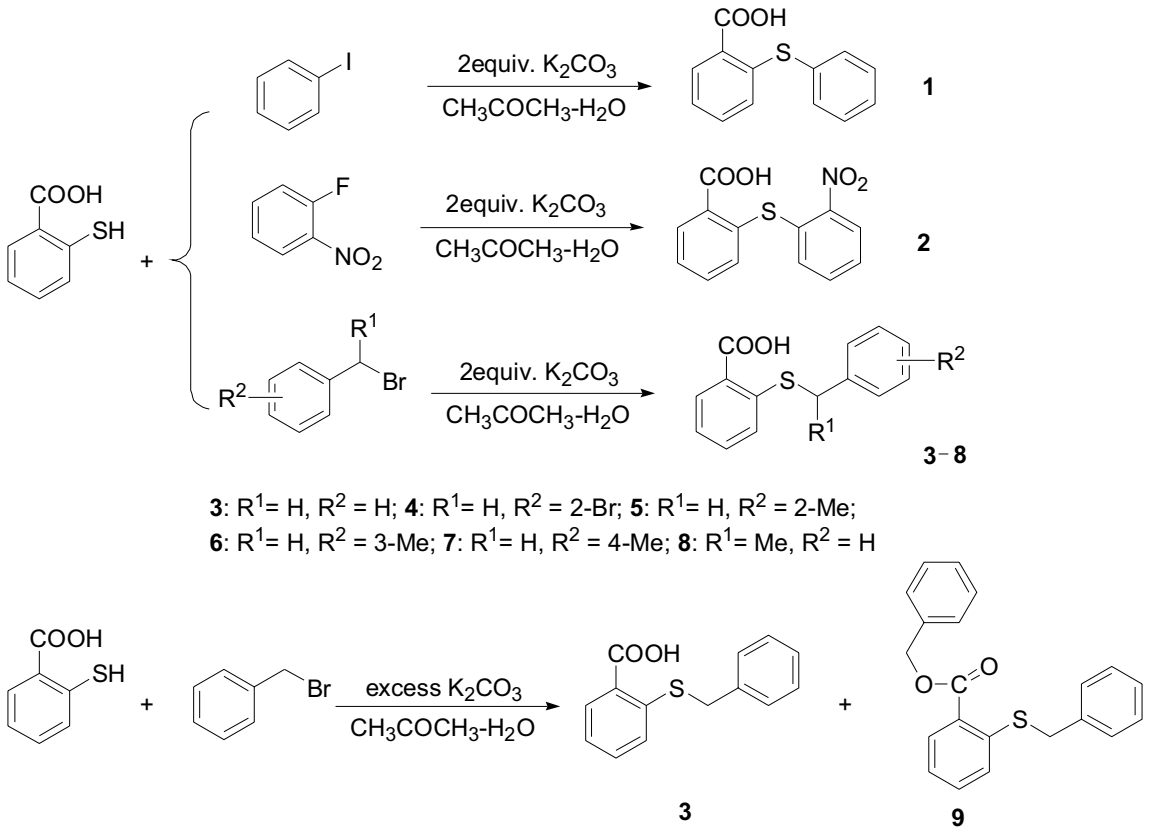
Introduction

In organic synthetic reactions, the scope and application of organosulfur chemistry has increased remarkably since sulfur-containing groups could serve as an important auxiliary function in synthetic sequences [1]. The preparation of aryl sulfides constitutes an active area of organosulfur chemistry due to the extensive biological and pharmaceutical applications of compounds containing C_{aryl}–S bonds [2, 3]. For example, aryl sulfide moieties are key components of commercial pharmaceuticals, including Lansoprazole, Sulindac, Esomeprazole, and Quetiapine. As a result, practical, cheap and efficient methods leading to C_{aryl}–S bond formation have attracted great attention [4–6]. Usually, synthesis of aryl sulfides involves the transition-metal-catalyzed cross-coupling of aryl halides with thiols with the assistance of a base [7, 8]. However, a number of transition-metal-free reactions for aryl sulfide preparations have also been reported [9–11]. On the other hand, thiosalicylic acid and its derivatives have received much interest in recent years due to their potential application in numerous disease treatments, in particular inflammatory, allergic and respiratory diseases [12–14]. For instance, copper(II) complexes with *S*-alkyl (alkyl = benzyl, methyl, ethyl, propyl, butyl) derivatives of thiosalicylic acid demonstrated moderate or selective antibacterial activity and low antifungal activity [14]. Herein, we report the syntheses and crystal structures of both diaryl thioethers and aryl benzyl thioethers by reacting thiosalicylic acid with aryl halides or benzyl halides in the presence of two equiv. K_2CO_3 without a transition metal, as shown in Scheme 1, and a thioether compound bearing a carboxylate group in the presence of excess base that has also been isolated and structurally characterized in this paper.

Experimental

General

All syntheses were carried out under nitrogen. Thiosalicylic acid, iodobenzene, benzyl bromide, 2-bromobenzyl bromide, 2-methylbenzyl bromide, 3-methylbenzyl bromide, 4-methylbenzyl bromide, (1-bromoethyl)-benzene, 1-fluoro-2-nitrobenzene and potassium carbonate were purchased from commercial sources and used without further purification. Thioethers were synthesized according to literature methods [15]. ^{1}H NMR spectra were recorded on a Bruker AM 400 spectrometer. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^{1}H). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer using KBr pellets. Gas chromatography analyses were performed with an FID detector on a Shimadzu GC-2010 Plus spectrometer using the RTX-5 column (15 m × 0.25 mm, film thickness 0.25 µm). The initial temperature of the column was 110 °C and increased to 260 °C with a rate of 20 °C min^{-1}.



Scheme 1 Syntheses of diaryl thioethers and aryl benzyl thioethers **1**–**9** derived from thiosalicylic acid

Synthesis of 2-Phenylsulfanyl-benzoic Acid (1)

A mixture of thiosalicylic acid (0.77 g, 5 mmol), iodobenzene (0.55 mL, 5 mmol), and K_2CO_3 (1.38 g, 10 mmol), in water–acetone (20 mL, v/v = 1:1) was stirred at reflux for 8 h. After cooling and extraction with water (10 mL) and ethyl acetate (10 mL), the aqueous phase was acidified to pH 7.0 with dilute HCl (1 M). The white precipitate was collected by filtration and washed with water, then dried to yield compound **1** as a white powder. Crystalline product of compound **1** was obtained by slow evaporation of a methanol–acetone solution at room temperature over a period of 5 days. Yield: 86%. GC: purity 100%, $t_R = 6.252$ min. IR (cm^{-1}): 3120, 1688 ν(–COOH). ^{1}H NMR (acetone-d_6) δ (ppm): 6.80 (d, $J = 8.4$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.32–7.36 (m, 1H), 7.49–7.57 (m, 5H), 8.00 (t, $J = 2.0$ Hz, 1H).

Synthesis of 2-(2-Nitro-phenylsulfanyl)-benzoic Acid (2)

The method was similar to that used for **1**, employing 1-fluoro-2-nitro-benzene (0.70 g, 5 mmol) instead of iodobenzene. Crystals suitable for X-ray analysis were grown by slow evaporation of methanol–acetone solution (v:v = 2:1) at room temperature over a period of 4 days. Yield: 89%. IR (cm^{-1}): 3128, 1689 ν(–COOH). ^{1}H NMR (acetone-d_6) δ (ppm): 7.25 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.40 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 7.52–7.61 (m, 4H), 8.01 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H), 8.20 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H).

Synthesis of 2-Benzylsulfanyl-benzoic Acid (3)

The method was similar to that used for **1**, employing benzyl bromide (0.85 g, 5 mmol) instead of iodobenzene. Yield: 94%. GC: purity 100%, $t_R = 6.493$ min. IR (cm^{-1}): 3120, 1693 ν(–COOH), 834 ν(–CH_2–S–). ^{1}H NMR (acetone-d_6) δ (ppm): 4.23 (s, 2H, –CH_2–S–), 7.21–7.52 (m, 8H), 7.98–8.05 (m, 1H).

Synthesis of 2-(2-Bromo-benzylsulfanyl)-benzoic Acid (4)

The method was similar to that used for **1**, employing 1-bromo-2-bromomethyl-benzene (1.25 g, 5 mmol) instead of iodobenzene. Yield: 99%. GC: purity 100%, $t_R = 7.437$ min. IR (cm^{-1}): 3124, 1689 ν(–COOH), 836 ν(–CH_2–S–). ^{1}H NMR (acetone-d_6) δ (ppm): 4.32 (s, 2H,

–CH_2S–), 7.21–7.27 (m, 2H), 7.32–7.38 (m, 1H), 7.49–7.64 (m, 4H), 8.02 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H).

Synthesis of 2-(2-Methyl-benzylsulfanyl)-benzoic Acid (5)

The method was similar to that used for **1**, employing 1-bromomethyl-2-methyl-benzene (0.92 g, 5 mmol) instead of iodobenzene. Crystals suitable for X-ray analysis were grown by slow evaporation of methanol–acetone solution (v:v = 2:1) at room temperature over a period of 4 days. Yield: 90%. GC: purity 100%, $t_R = 7.147$ min. IR (cm^{-1}): 3118, 1687 ν(–COOH), 835 ν(–CH_2–S–). ^{1}H NMR (acetone-d_6) δ (ppm): 2.41 (s, 3H, –CH_3) 4.26 (s, 2H, –CH_2S–), 7.22–7.63 (m, 7H), 8.01 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H).

Synthesis of 2-(3-Methyl-benzylsulfanyl)-benzoic Acid (6)

The method was similar to that used for **1**, employing 1-bromomethyl-3-methyl-benzene (0.92 g, 5 mmol) instead of iodobenzene. Crystals suitable for X-ray analysis were grown by slow evaporation of methanol–acetone solution (v:v = 2:1) at room temperature over a period of 5 days. Yield: 85%. GC: purity 100%, $t_R = 7.143$ min. IR (cm^{-1}): 3120, 1688 ν(–COOH), 838 ν(–CH_2–S–). ^{1}H NMR (acetone-d_6) δ (ppm): 2.39 (s, 3H, –CH_3) 4.25 (s, 2H, –CH_2S–), 7.22–7.62 (m, 7H), 8.02 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H).

Synthesis of 2-(4-Methyl-benzylsulfanyl)-benzoic Acid (7)

The method was similar to that used for **1**, employing 1-bromomethyl-4-methyl-benzene (0.92 g, 5 mmol) instead of iodobenzene. Crystals suitable for X-ray analysis were grown by slow evaporation of methanol–acetone solution (v:v = 2:1) at room temperature over a period of 4 days. Yield: 86%. GC: purity 100%, $t_R = 7.145$ min. IR (cm^{-1}): 3120, 1686 ν(COOH), 832 ν(–CH_2–S–). ^{1}H NMR (acetone-d_6) δ (ppm): 2.40 (s, 3H, –CH_3) 4.24 (s, 2H, –CH_2S–), 7.22–7.62 (m, 7H), 8.02 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz, 1H).

Table 1 Crystallographic data and experimental details for **2**, **5**–**7**, and **9** [20]

Compound	2	5	6	7	9
CCDC number	1556494	1556495	1828744	1828743	1556496
Empirical formula	$C_{13}H_9NO_4S$	$C_{15}H_{14}O_2S$	$C_{15}H_{14}O_2S$	$C_{15}H_{14}O_2S$	$C_{21}H_{18}O_2S$
Formula weight	275.27	258.32	258.32	258.32	334.41
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic
a (Å)	12.04(3)	5.4334(14)	15.1881(12)	14.934(13)	5.662(7)
b (Å)	7.311(19)	7.7787(19)	7.3288(6)	5.116(5)	11.988(15)
c (Å)	14.22(4)	16.488(4)	23.7366(19)	33.76(3)	12.959(15)
α(°)	90	76.601(3)	90	90	72.796(15)
β (°)	93.94(3)	86.078(3)	90	91.523(12)	86.431(15)
γ (°)	90	70.772(3)	90	90	89.971(15)
V ($Å^3$)	1248(6)	640.0(3)	2642.1(4)	2578(4)	838.6(18)
Space group	$P2_1/n$	*P*-1	*Pbca*	*C*2/*c*	*P*-1
Z	4	2	8	8	2
D_{calc} (g cm^{-3})	1.465	1.340	1.299	1.331	1.324
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)
F(000)	568	272	1088	1088	352
μ(Mo-Kα) (mm^{-1})	0.268	0.243	0.236	0.241	0.203
Total refln	6051	3989	15,685	6565	5132
Independent refln	2675	2838	2997	2352	3648
R_{int}	0.0309	0.0123	0.0360	0.2226	0.0252
*R*1[a], *wR*2[b] ($I > 2\sigma(I)$)	0.0495, 0.1432	0.0345, 0.0956	0.0377, 0.1142	0.0651, 0.1499	0.0541, 0.1325
*R*1, *wR*2 (all data)	0.1379, 0.2240	0.0411, 0.1014	0.0581, 0.1395	0.0881, 0.1815	0.1148, 0.1648
GoF[c]	1.210	1.048	0.861	0.878	1.009

[a] $R1 = \sum |F_o| - |F_c| / \sum |F_o|$

b $wR2 = \left[\sum w \left(|F_o^2| - |F_c^2| \right)^2 / \sum w |F_o^2|^2 \right]^{1/2}$

c $GoF = \left[\sum w \left(|F_o| - |F_c^2| \right)^2 / (N_{obs} - N_{param}) \right]^{1/2}$

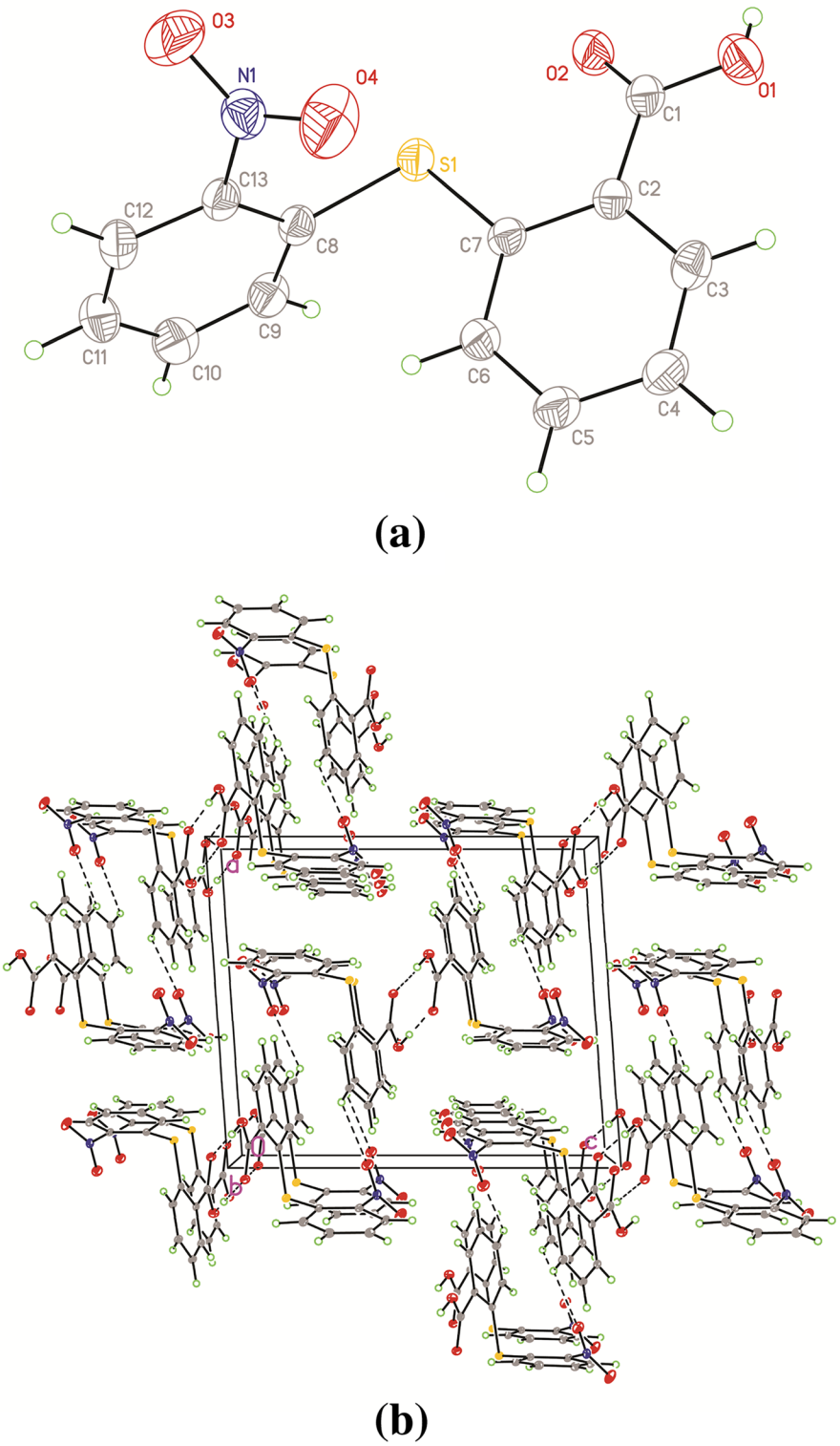
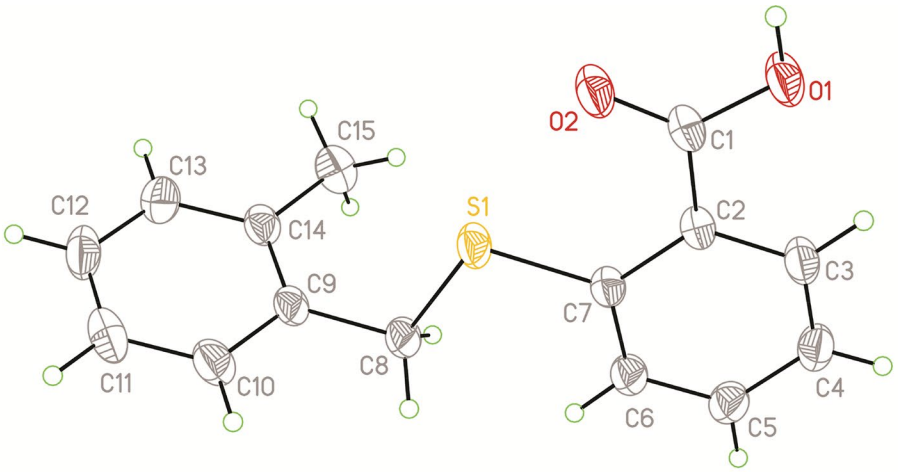


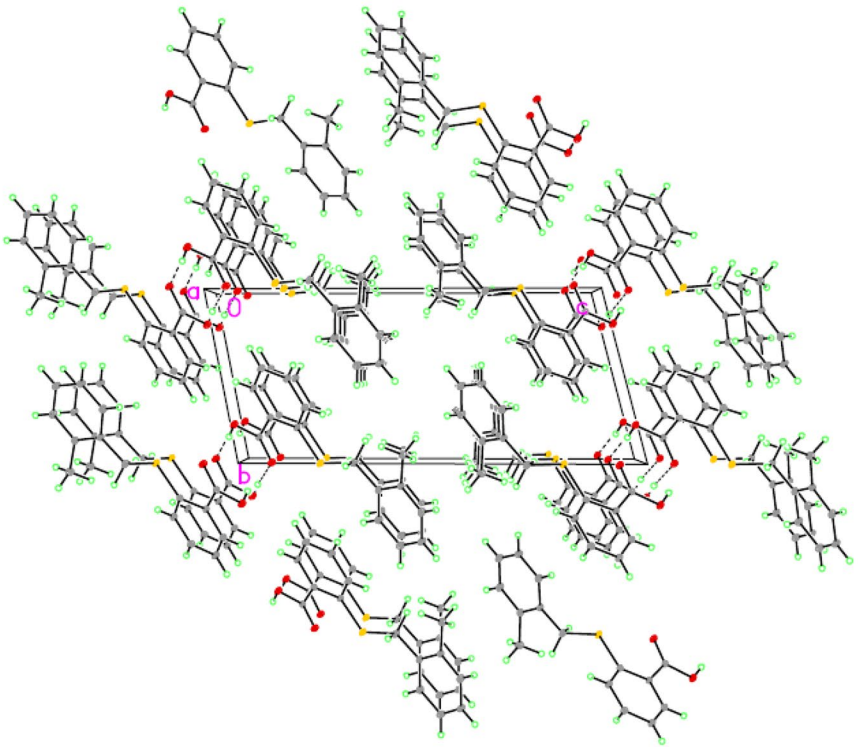
Fig. 1 **a 2**, showing the atom-labelling scheme of one molecule in the asymmetric unit. Displacement ellipsoids are drawn at the 40% probability level. **b** 2D framework of **2**, projected along the crystallographic *b* axis. O–H···O and C–H···O hydrogen bonds are shown as dashed lines

Synthesis of 2-(1-Phenyl-ethylsulfanyl)-benzoic Acid (8)

The method was similar to that used for **1**, employing (1-bromo-ethyl)-benzene (0.92 g, 5 mmol) instead of iodobenzene. Yield: 84%. GC: purity 100%, $t_R = 6.621$ min. IR (cm^{-1}): 3117, 1688 ν(–COOH), 835 ν(–CH_2–S–). ^{1}H NMR (acetone-d_6) δ (ppm): 1.61 (d, $J = 6.8$ Hz, 3H, –CH(CH_3), 4.68 (q, $J = 6.8$ Hz, 1H, –CH(CH_3)), 7.18–7.50 (m, 8H), 7.89 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H).



(a)

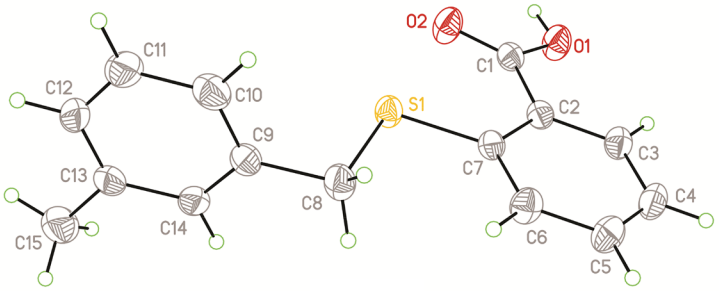


(b)

Fig. 2 **a** The content of **5**, showing the atom-labeling scheme of one molecule in the asymmetric unit. Displacement ellipsoids are drawn at the 40% probability level. **b** View showing the formation of the centrosymmetric dimer through O–H···O hydrogen bonds in the molecular packing projected along the crystallographic *a* axis

Synthesis of 2-Benzylsulfanyl-benzoic Acid Benzyl Ester (9)

A mixture of thiosalicylic acid (0.77 g, 5 mmol), benzyl bromide (0.85 g, 5 mmol), and K_2CO_3 (1.38 g, 20 mmol), in water–acetone (20 mL, v/v = 1:1) was stirred at reflux for 24 h. After cooling overnight, colorless crystals precipitated. The crystals were collected by filtration and washed with water, then dried to yield compound **9**. Crystals suitable for X-ray analysis were grown by slow evaporation of methanol–acetone solution (v:v = 2:1) at room temperature over a period of 5 days. The crystal structure of this compound has been reported previously [20] and is included for the sake of comparison only. Yield: 49%. IR (cm^{-1}): 1720 ν(–COOR), 838 ν(–CH_2–S–). ^{1}H NMR (acetone-d_6) δ (ppm): 4.23 (s, 2H, –CH_2S–), 4.30 (s, 2H, –CH_2O–), 7.20–7.54 (m, 13H), 7.98–8.07 (m, 1H).



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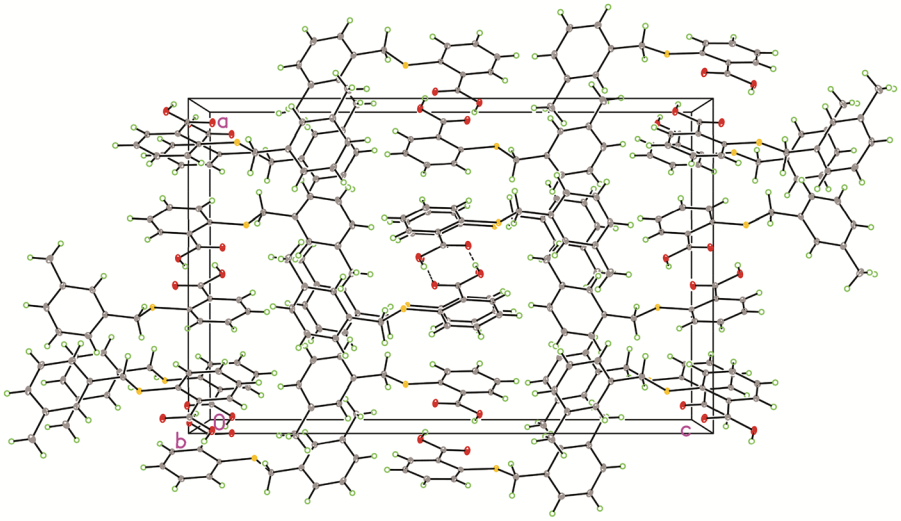


(b)

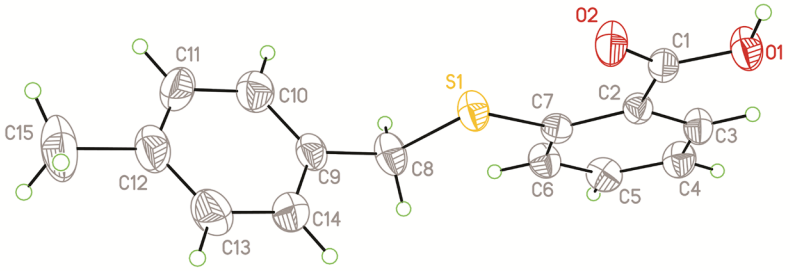
Fig. 3 **a** The content of **6**, showing the atom-labeling scheme of one molecule in the asymmetric unit. Displacement ellipsoids are drawn at the 40% probability level. **b** View showing the formation of the centrosymmetric dimer through O–H···O hydrogen bonds in the molecular packing projected along the crystallographic *b* axis

X-ray Crystallography

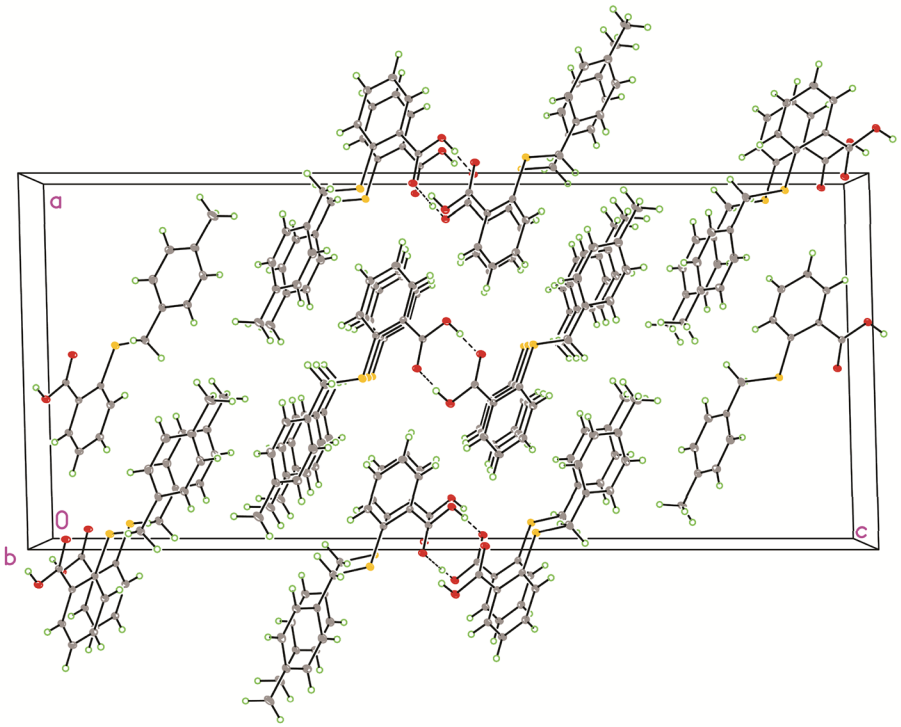
Crystallographic data and experimental details for **2**, **5**–**7** and **9** [20] are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 2 CCD diffractometer using graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) at 296(2) K. The collected frames were processed with the software SAINT [16]. The data was corrected for absorption using the program SADABS [17]. Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [18]. All non-hydrogen atoms were refined anisotropically. The carboxylic acid hydrogens in compounds **2**, **5**, **6** and **7** are located in the diffraction maps. The positions of all other hydrogen atoms were generated geometrically (C_{sp3}–H = 0.96 Å and C_{sp2}–H = 0.93 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement.

Results and Discussion

As shown in Scheme 1, reactions of thiosalicylic acid and iodobenzene or 1-fluoro-2-nitro-benzene in the presence of two equiv. of K_2CO_3 in acetone–water at reflux for 8 h afforded crystalline solid diaryl thioethers **1** and **2** in good yields. Treatment of thiosalicylic acid with benzyl bromide or the bromo/methyl substituted benzyl bromide compounds under the same conditions afforded corresponding aryl benzyl thioether derivatives **3**–**8** in excellent yields (85–99%). Similar reactions of thiosalicylic acid with benzyl bromide in the presence of excess K_2CO_3 gave benzyl 2-(benzylsulfanyl)benzoate **9** through further esterification of the carboxyl group. Compared to the previously reported reaction between thiosalicylic acid and 1-chloro-2-nitro-benzene to synthesize compound **2**, the yield is improved from 53 to 89% in this report [15]. Moreover, a similar compound, 2-(2-methoxyphenylsulfanyl)-benzoic acid, was synthesized by an alternative method, from reactions of 2-methoxythiophenol and 2-chlorobenzoic acid with K_2CO_3 as the base and copper as the catalyst [19]. It is noted that compound **9** has already been synthesized and characterized by an



(a)

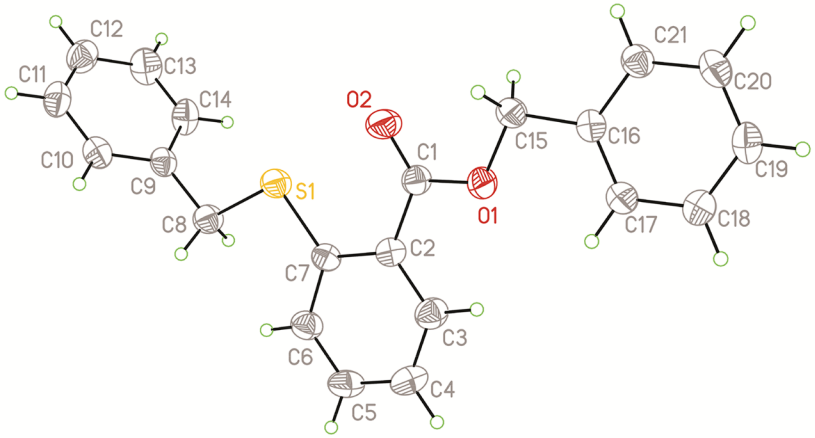


(b)

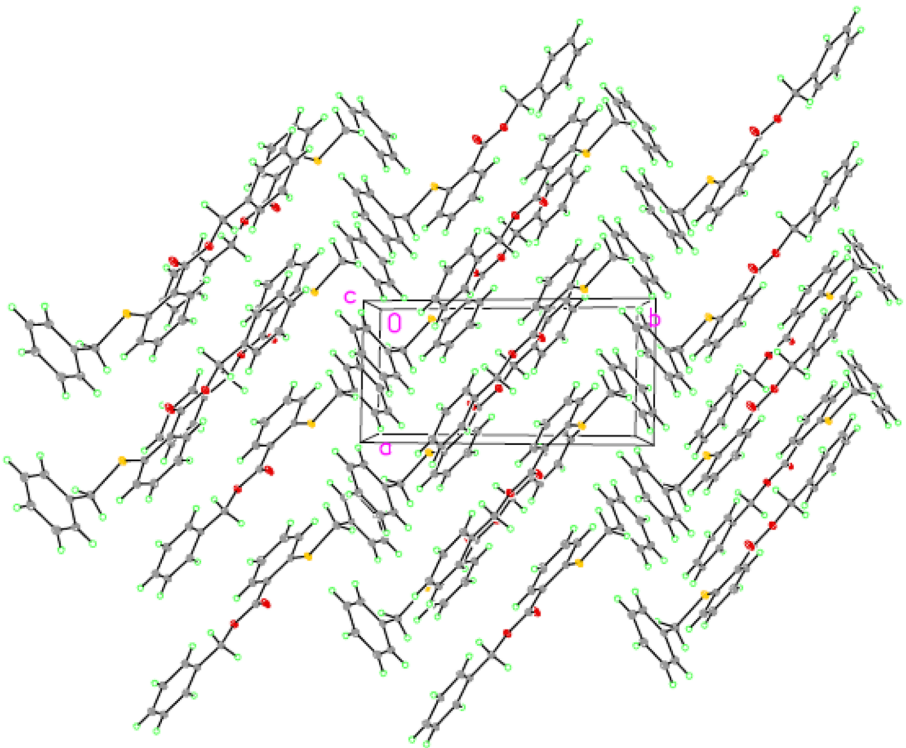
Fig. 4 **a** The content of **7**, showing the atom-labeling scheme of one molecule in the asymmetric unit. Displacement ellipsoids are drawn at the 40% probability level. **b** View showing the formation of the centrosymmetric dimer through O–H···O hydrogen bonds in the molecular packing projected along the crystallographic *b* axis

alternative method using thiosalicylic acid to react with two equiv. of benzyl halogenide in the presence of two equiv. of NaOH [20]. The infrared spectra of thioether compounds **1**–**8** with carboxyl groups showed $–CO_2H$ peaks at about 3120 and 1690 cm^{-1}, and for ester derivative **9** showed a $–CO_2R$ peak at about 1720 cm^{-1}. The aryl benzyl thioethers **3**–**9** showed $–CH_2–S–$ or $–CH(CH_3)–S$-peaks at around 835 cm^{-1} [21]. The ^1H NMR spectra of compounds **3**–**7** and **9** all showed $–CH_2–S–$ protons as a single peak ranging from 4.23 to 4.32 ppm, which are comparable to those in related compounds [22]. The signal of a $–CH(CH_3)–S–$ proton showed a quartet at 4.68 ppm with $J = 6.8$ Hz, while the $–CH(CH_3)–S–$ protons showed a doublet at 1.61 ppm with $J = 6.8$ Hz. GC analysis showed that the retention time of aryl benzyl thioethers **3**–**8** (6.493–7.437 min) was longer than that of diaryl thioether **1** (6.252 min), and the isomers of **5**–**7** have almost the same retention time (7.143–7.147 min) indicating that *o*-, *m*-, or *p*-positions of a methyl group have little effect on the retention time of similar compounds.

Molecular structures of compounds **2**, and **5**–**7** were further confirmed by single-crystal X-ray diffraction analysis, as shown in Figs. 1, 2, 3, 4 and 5, respectively. Selected bond lengths and angles are given in Tables 2, 3, 4, 5 and 6, while the hydrogen-bond characteristics and geometric parameters for **2**, **5**, **6** and **7** are summarized in Table 7. The C(7)–S(1) bond length is 1.779(6) Å in **2**, which lies well in the range of those in analogous compounds, 2-(2-methoxyphenylsulfanyl)-benzoic acid (1.782 Å) [19], 2-[2-(hydroxy-isopropoxy-phosphoryl)-phenylsulfanyl]-benzoic acid (1.774 Å) [23], 2-(4-trifluoromethyl-phenylsulfanyl)-benzoic acid (1.782 Å) [24], and the same structure reported by Reinke (1.789 Å) [25]. In aryl benzyl thioether isomers **5**–**7**, the C_{Ar}–S bond



(a)



(b)

Fig. 5 **a** Molecular structure of **9** [20], showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level. **b** Packing mode of compound **9**, projected along the crystallographic *c* axis

Table 2 Selected bond lengths (Å) and angles (°) for **2**

S(1)–C(7)	1.779(6)	S(1)–C(8)	1.784(5)
C(1)–O(1)	1.313(5)	C(1)–O(2)	1.218(5)
N(1)–O(3)	1.204(5)	N(1)–O(4)	1.187(5)
C(1)–C(2)	1.473(5)	N(1)–C(13)	1.477(6)
C(7)–S(1)–C(8)	101.62(15)	O(1)–C(1)–O(2)	123.4(4)
O(3)–N(1)–O(4)	123.6(4)		

Table 3 Selected bond lengths (Å) and angles (°) for **5**

S(1)–C(7)	1.7707(14)	S(1)–C(8)	1.8275(15)
C(1)–O(1)	1.3140(17)	C(1)–O(2)	1.2221(17)
C(8)–C(9)	1.507(2)	C(1)–C(2)	1.480(2)
C(7)–S(1)–C(8)	102.28(7)	O(1)–C(1)–O(2)	122.33(14)
C(9)–C(8)–S(1)	108.39(10)		

Table 4 Selected bond lengths (Å) and angles (°) for **6**

S(1)–C(7)	1.7640(19)	S(1)–C(8)	1.822(2)
C(1)–O(1)	1.318(2)	C(1)–O(2)	1.222(2)
C(8)–C(9)	1.508(3)	C(1)–C(2)	1.474(3)
C(7)–S(1)–C(8)	103.64(9)	O(1)–C(1)–O(2)	121.98(18)
C(9)–C(8)–S(1)	105.72(13)		

Table 5 Selected bond lengths (Å) and angles (°) for **7**

S(1)–C(7)	1.759(3)	S(1)–C(8)	1.808(3)
C(1)–O(1)	1.303(3)	C(1)–O(2)	1.217(3)
C(8)–C(9)	1.498(4)	C(1)–C(2)	1.477(4)
C(7)–S(1)–C(8)	102.26(14)	O(1)–C(1)–O(2)	122.5(3)
C(9)–C(8)–S(1)	108.7(2)		

Table 6 Selected bond lengths (Å) and angles (°) for **9** [20]

S(1)–C(7)	1.732(3)	S(1)–C(8)	1.797(3)
C(1)–O(1)	1.317(3)	C(1)–O(2)	1.192(3)
C(15)–O(1)	1.434(3)	C(15)–C(16)	1.489(4)
C(8)–C(9)	1.479(4)	C(1)–C(2)	1.474(4)
C(7)–S(1)–C(8)	103.26(12)	O(1)–C(1)–O(2)	122.4(2)
O(1)–C(15)–C(16)	108.9(2)	C(16)–C(15)–S(1)	107.68(18)

lengths are 1.7707(14), 1.7640(19) and 1.759(3) Å, respectively, a little shorter than the corresponding C_{Bn}–S bond lengths [1.8275(15) Å for **5**, 1.822(2) for **6**, 1.808(3) Å for **7**]. The C_{Ar}–S and C_{Bn}–S bond lengths are 1.732(3) and 1.797(3) Å, respectively in **9**, which are slightly shorter than those in the known compound benzyl 2-(benzylsulfanyl)benzoate reported by Leka (1.7623(19), 1.8159(18) Å) [20]. The C_{Ar}–S–C_{Ar} bond angle is 101.57(14)° in diaryl thioether **2**, which is near to those in aryl benzyl thioethers **5** (102.28(7)°), **6** (103.64(9)°), **7** (102.26(14)°) and **9** (103.26(12)°). As expected, the C–O bond lengths (1.303(3)–1.318(2) Å) are a little longer than the C=O bond lengths (1.217(3)–1.2221(17) Å) in carboxylic acid compounds **2**, **5**, **6** and **7**. Similarly, the C–O bond length of 1.317(3) Å is longer than the C=O bond length (1.192(3) Å) in carboxylate compound **9** [20]. In diaryl thioether **2**, the carboxylic acid group (C2/C1/O2/O1) is twisted by 15.5(2)° from the mean plane of the adjacent benzene ring (C2–C7), similar to that in 2-(4-trifluoromethyl-phenylsulfanyl)-benzoic acid (13.6(7)°) [24]. While in aryl benzyl thioether molecules **5**–**7** and **9**, the carboxylic acid group are twisted by 2.5(1)° for **5**, 5.4(1)° for **6**, and 2.5(2)° for **7**, and 3.2(2)° for **9** [20] from the mean plane of C2–C7. In compound **2**, the two phenyl ring planes are roughly perpendicular (86.0(2)°), similar to that in 2-(4-trifluoromethyl-phenylsulfanyl)-benzoic acid (88.7(2)°) [24], but larger than that in 2-(2-methoxyphenylsulfanyl)-benzoic acid (78.50(12)°) [19], suggesting the free rotation of the *S*-phenyl ring around the single bonds of the C(7)–S(1)–C(8) fragment. In aryl benzyl thioether molecules **5**–**7**, the dihedral angles between the mean planes of the phenyl rings are 74.5 (1)° for **5**, 87.0(1)° for **6** and 78.3(1)° for **7**. In compound **9** [20], the dihedral angle between the central thiosalicylic ring C2–C7 and terminal *O*-benzyl group is 5.8(2)° indicating a nearly coplanar orientation of these two fragments. On the other hand, the ring of the *S*-benzyl group is significantly twisted with respect to the central ring C2–C7 forming a dihedral angle of 71.6(1)°. The dihedral angle between the peripheral phenyl rings in **9** is 65.78(10)°, as expected similar to that in benzyl 2-(benzylsulfanyl)benzoate reported by Leka (66.16(6)°) [20].

The packing view of compound **2** along the *ac* plane is shown in Fig. 1b. Crystal packing in molecule **2** is governed by the weak intermolecular C–H···O(NO_2) and O–H···O hydrogen-bonding interactions (Table 7). In the crystal structure of **2**, the H-bonded layers are parallel to (1 0 − 1) (Fig. 1). The separation of H(1)···O(2) is 1.92(5) Å and the angle of O(1)–H(1)···O(2) is 167(5)° in compound **2**, and comparable with those in the molecules of 2-(4-trifluoromethyl-phenylsulfanyl)-benzoic acid (1.86 Å, 175°) [24] and 2-(2-methoxyphenylsulfanyl)-benzoic acid (1.85 Å, 171°) [19]. In compounds **5**–**7**, symmetry equivalent molecules related by a crystallographic inversion center are linked by O–H···O hydrogen bonds, forming centrosymmetric dimers as shown in Figs. 2b, 3b and 4b, respectively. The separation of H(1)···O(2) is 1.79(3) Å and the angle of O(1)–H(1)···O(2) is 174(2)° for **5**, similar to those in its isomers **6** (1.74(3) Å, 176(3)°) and **7** (1.78(5) Å, 167(5)°).

Table 7 Hydrogen-bonding system for **2**, and **5**–**7**

Compound	D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (deg)
2	O(1)–H(1)···O(2)^{i}	0.76(5)	1.92(5)	2.664(6)	167(5)
	C5A–H5AO4D	0.930	2.543	3.211	129.1
5	O(1)–H(1)···O(2)^{ii}	0.89(2)	1.79(3)	2.6734(17)	174(2)
6	O(1)–H(1)···O(2)^{iii}	0.91(3)	1.74(3)	2.649(2)	176(3)
7	O(1)–H(1)···O(2)^{iv}	0.90(5)	1.78(5)	2.661(3)	167(5)

Symmetry codes: (i) −x+1, −y+3, −z+1; (ii) −x−1, −y+2, −z; (iii) −x+1, −y+3, −z+1; (iv) −x+2, −y−1, −z+1

No obvious hydrogen bonding interactions were found in the carboxylate compound **9** [20].

In summary, a series of diaryl thioethers and aryl benzyl thioethers were synthesized in excellent yields and characterized by single-crystal X-ray diffraction along with spectroscopic methods, in which a thioether compound with the ester group, 2-benzylsulfanyl-benzoic acid benzyl ester, was isolated from reactions of thiosalicylic acid and benzyl bromide in the presence of excess K_2CO_3. The dihedral angle of two phenyl rings in diaryl thioether **2** (86.0(2)°) is comparable to those in aryl benzy thioethers **5**–**7** (74.5(1)° for **5**, 87.0(1)° for **6** and 78.3(1)° for 7) and **9** (71.6(1)°) [20]. The carboxylic acid group (C2/C1/O2/O1) is twisted by 15.5(2)° from the mean plane of the adjacent phenyl ring (C2–C7) in diaryl thioether **2**, larger than those in aryl benzyl thioethers **5**–**7** and **9** (2.5(1)°–5.4(1)°) [20]. In the crystal structures of **5**–**7**, symmetry equivalent molecules are linked by O–H···O hydrogen bonds, forming centrosymmetric dimers [19], whereas the crystal packing in **2** displays a hydrogen-bonded two-dimensional framework displaying different types of O–H···O and C–H···O(NO_2) hydrogen bonds.

Supplementary material

Crystallographic data for **2**, **5**–**7** and **9** [20] has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1556494, 1556495, 1828744, 1828743, and 1556496 respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1233-336-033; e-mail: deposit@ccdc.cam.ac.uk].

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