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Short Note

2,2′-Trisulfanediyldibenzoyl Chloride

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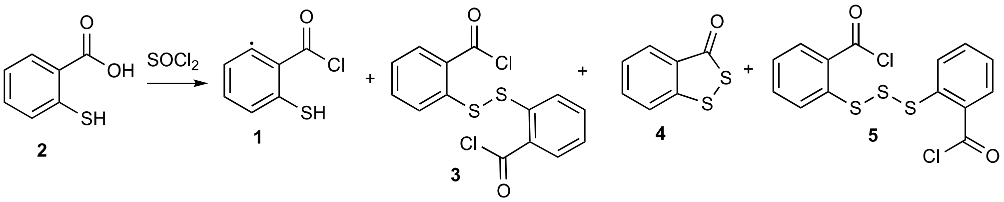
Abstract: The X-ray structure of the title compound, formed at low conversion in the reaction of thiosalicylic acid with thionyl chloride, has been determined. The acid chloride groups are oriented to permit an attractive non-bonding O. . .S interaction. Mechanisms are suggested for the formation of this unexpected product. ^{1}H and ^{13}C NMR data are also reported for the first time for the major reaction product, 2-mercaptobenzoyl chloride.

Keywords: X-ray structure; trisulfane; chalcogen–chalcogen interaction; acid chloride

1. Introduction

Although 2-mercaptobenzoyl chloride **1** (Scheme 1) was first described in 1946 [1], with further reports in 1965 [2] and 1972 [3], it has only been characterised by its melting and boiling points, and no spectroscopic data have ever been documented. Even in recent papers, where it has been used to prepare compounds with medicinal [4] and material [5] applications, 2-mercaptobenzoyl chloride is generated and used directly, with no characterisation. We have investigated this problem and found that the treatment of thiosalicylic acid **2** with thionyl chloride gives various mixtures of products, including **1**, for which NMR data could be obtained for the first time. However, in one experiment, a by-product formed in very low yield was identified by X-ray diffraction as an unusual diaryltrisulfane (trisulfide), the structure and mechanism of formation of which are discussed herein.



Scheme 1. Products obtained from the reaction of **2** with SOCl$_2$.

2. Results

The reaction of thiosalicylic acid **2** with thionyl chloride under a variety of different reaction conditions gave mixtures of moisture-sensitive products, which were subjected to separation by distillation or recrystallisation. Whilst it was difficult to achieve complete separation, comparison of the spectra obtained for varying mixtures allowed the unambiguous assignment of ^{1}H and ^{13}C NMR spectra for 2-mercaptobenzoyl chloride **1**, 2,2′-dithiodibenzoyl chloride **3** and benzo[*c*][1,2]dithiol-3-one **4**. The treatment of **2** with thionyl chloride, either in the presence or absence of CH$_2$Cl$_2$, followed by evaporation and vacuum distillation, gave mixtures of **1** and **4** and left the less volatile dichloride **3** as a residue. Further distillation resulted in enrichment in **1** as compared to **4** and the final mixture, obtained in 54% overall yield from **2**, consisted of 80% **1** and 20% **4** allowing the required NMR data to be obtained. The data for **3** [6,7] and **4** [8] were in agreement

Citation: Aitken, R.A.; Campbell, A.H.; Fletcher, C.E.; Slawin, A.M.Z. 2,2′-Trisulfanediyldibenzoyl Chloride. *Molbank* **2023**, *2023*, M1731. https://doi.org/10.3390/M1731

Academic Editor: Rodrigo Abonia

Received: 8 August 2023
Revised: 17 September 2023
Accepted: 19 September 2023
Published: 21 September 2023

with reported values, and the new data for **1** are given in the Experimental section (see Supplementary Materials).

In the hope of being able to determine the structure of **1** by X-ray diffraction, small crystals obtained in a separate experiment, by cooling a saturated solution of **2** in thionyl chloride, were examined and, quite unexpectedly, these proved to be the symmetrical trisulfane: 2,2′-trisulfanyldibenzoyl chloride **5** (Figure 1). It should be noted that this compound was obtained in very low yield, meaning that no physical or spectroscopic data could be recorded, but the structure obtained shows some interesting features.

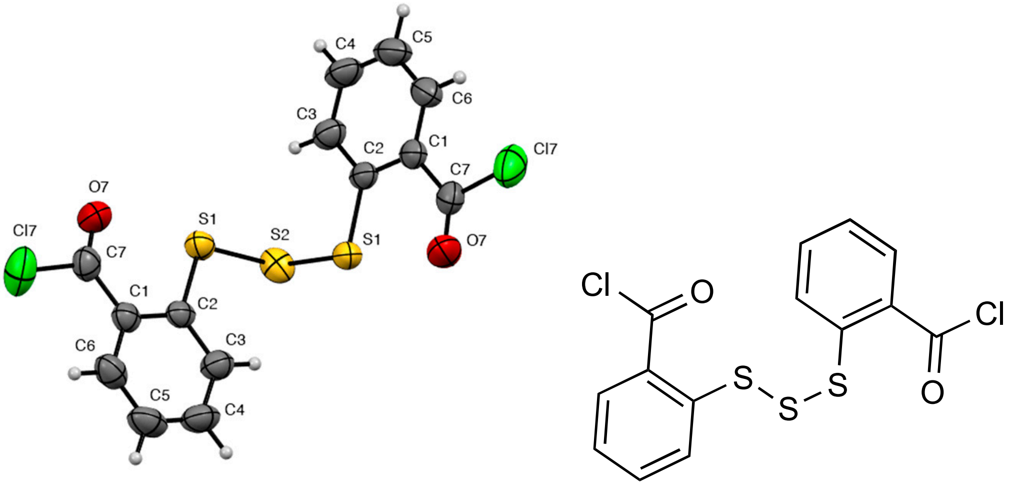


Figure 1. The molecular structure of **5**, showing anisotropic displacement ellipsoids drawn at a 50% probability level, and the numbering system used.

Only a few symmetrical trisulfanes appear to have been crystallographically characterised before (Figure 2), and a summary of the key geometric parameters (Table 1) shows that both the S–S bond length and angles at sulfur in compound **5** are in good agreement with the previously reported structures of **6–12** [9–15].

Table 1. Comparison of selected geometric parameters for symmetrical trisulfanes R–S–S–S–R.

Compd	CSD Refcode	S–S Length (Å)	S–S–S Angle (°)	C–S–S angle (°)	Ref
5	—	2.047(1)	107.39(7)	104.8(1)	This work
6	LEBFOP	2.058(2)	105.3(1)	103.85(14)	[9]
7	NUBYIV	2.023(4), 2.021(4)	106.9(1)	103.5(3), 103.3(3)	[10]
8	PEKYOT	2.066(1), 2.057(1)	112.54(3)	112.05(7), 111.15(7)	[11]
9 *	XOSBEM	2.0503(5), 2.0426(5)	107.64(2)	103.63(5), 101.82(5)	[12]
9 *	XOSBEM	2.0513(5), 2.0418(6)	107.99(2)	103.61(5), 101.41(5)	[12]
10	RIKXIS	2.0412	106.75	99.93	[13]
11	UBIVUW	2.047(1), 2.039(2)	110.53(5)	107.1(1), 105.6(1)	[14]
12	CAFFAQ	2.0159, 2.0304	107.58	104.30, 102.07 §	[15]

* Two independent molecules. § Ge–S–S.

The molecular structure of **5** is perfectly symmetrical and the two acid chloride groups are oriented to allow significant non-bonding (peripheral) S. . .O (carbonyl) interactions (Figure 3). In fact this is in excellent agreement with the pattern observed in structures of **3** and the monosulfide **13** over 40 years ago [16].

As shown in Figure 4 and Table 2, the structures of both **5** and **3** have short O. . .S distances (sum of Van der Waals radii: 3.32 Å) and O. . .S–S angles of almost 180°. In the case of the sulfide **13,** it is only geometrically possible for one of the two acid chloride groups to be oriented in this way, and the ring bearing the other is almost orthogonal, leading to a much weaker interaction with sulfur.

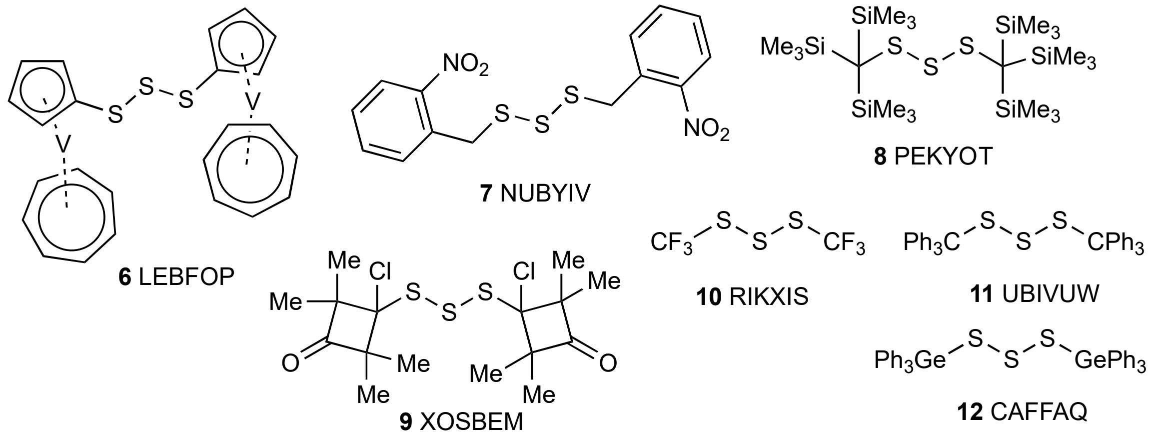


Figure 2. Examples of previously reported structurally characterised symmetrical trisulfanes with CSD Refcodes.

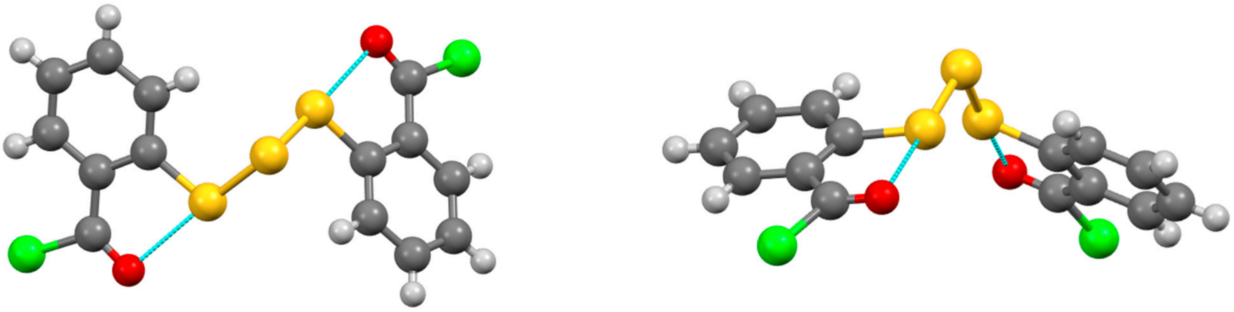


Figure 3. The molecular structure of **5**, showing non-bonding C=O. . .S interactions (dark grey–carbon, light grey–hydrogen, red–oxygen, yellow–sulfur, green–chlorine).

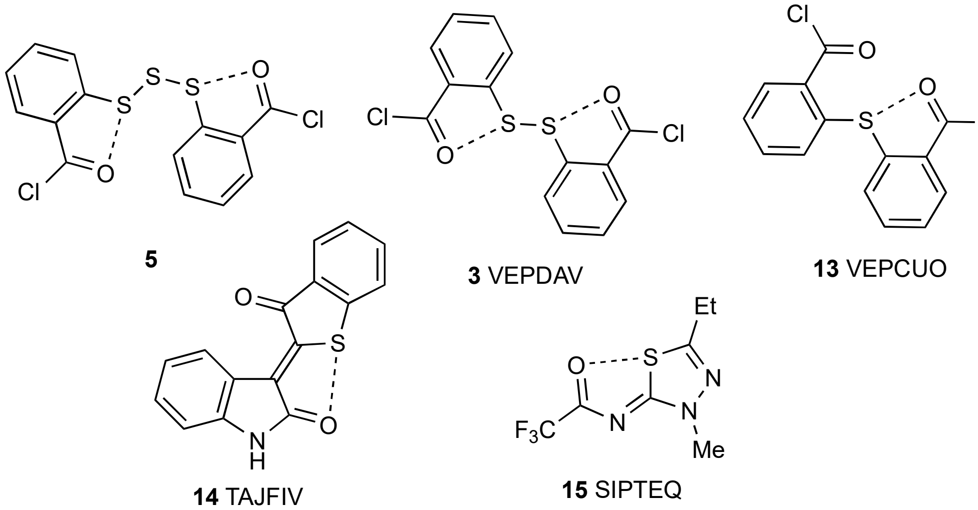


Figure 4. Non-bonding S. . .O interactions in **5**, **3** and **13–15**.

As described in a recent review [17], these interactions can be considered as partial sulfur–oxygen bonds and are comparable to those observed in thioindirubin **14** [18] and the acyliminothiadiazoline **15** [19].

Table 2. O. . .S interactions in compounds **5**, **3** and **13–15**.

	O. . .S Distance	O. . .S–X Angles	CSD Refcode	Ref
5	2.641(3)	173.46	—	This work
3 *	2.653(3), 2.664(3)	171.78(8), 173.99(8)	VEPDAV	[16]
3 *	2.654(3)	177.19(8)	VEPDAV	[16]
13	2.941(4) 2.727(3)	77.1(1), 173.7(2)	VEPCUO	[16]
14	2.700(1)	169.65(6)	TAJFIV	[18]
15	2.670(4)	160.0(2)	SIPTEQ	[19]

* Two independent molecules.

Despite its low yield, the mechanism by which compound **5** was formed is of some interest. We have been able to find two literature precedents for such a process. In the most similar case, 1,2-dihydro-2-thioxopyridine-3-carboxylic acid (which can be formulated as 2-mercaptopyridine-3-carboxylic acid and is, thus, the direct aza analogue of **2**) reacts with thionyl chloride to give a mixture of di- and tri-sulfanediyldiacid chlorides [20]. In the other, a range of substituted thiophenols react with thionyldiimidazole to give mixtures of diaryl disulfides and diaryl trisulfides [21]. With these processes in mind, we suggest that the formation of **5** may involve either oxidative coupling of **1** under the influence of thionyl chloride to give **3** and sulfur dichloride, which then reacts with **1** to give **5** (Figure 5); or, alternatively, it may proceed via stepwise formation of the trisulfane 2-oxide, which is then deoxygenated with concomitant formation of chlorine.

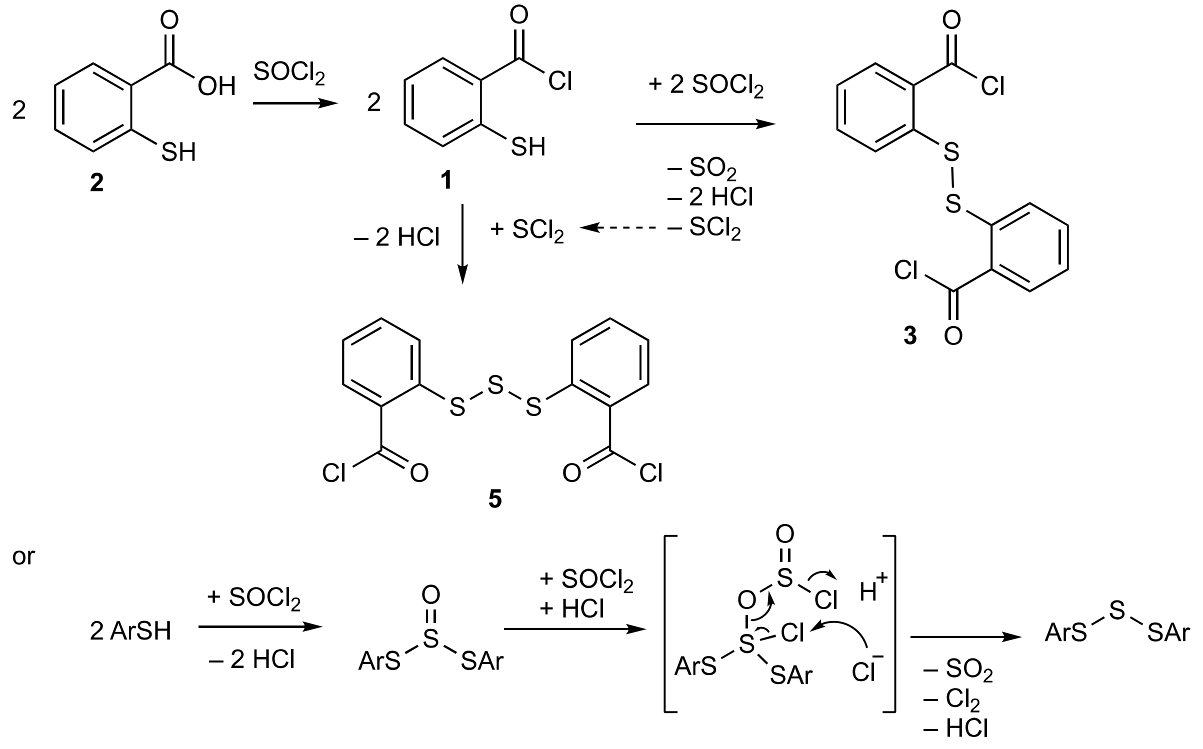


Figure 5. Possible routes for the formation of product **5**.

3. Experimental

NMR spectra were obtained for ^{1}H at 400 MHz and for ^{13}C at 125 MHz, using Bruker AV-II and AV-III instruments, respectively (Bruker, Billerica, MA, USA). Spectra were run at 25 °C on solutions in $CDCl_3$ with internal Me_4Si as the reference. Chemical shifts are reported in ppm to high frequency of the reference, and coupling constants *J* are in Hz. The HRMS measurement was performed using a Micromass instrument via electrospray ionisation.

3.1. Preparation of 2-Mercaptobenzoyl Chloride to Obtain NMR Data

A mixture of thiosalicylic acid (4.0 g, 26 mmol) and thionyl chloride (9.2 mL, 15.1 g, 127 mmol) was heated under reflux under nitrogen for 3.5 h. The excess of thionyl chloride was evaporated under reduced pressure, and the residue was Kugelrohr distilled twice under reduced pressure to give a solid (2.4 g, 54%) that was a 1:4 mixture of benzo[*c*][1,2-dithiol-3-one **4** and 2-mercaptobenzoyl chloride **1**.

Benzo[*c*][1,2]-dithiol-3-one **4:** d_H (400 MHz) 7.95 (1H, ddd, *J* 8.0, 1.2, 0.8), 7.67–7.62 (2H, m) and 7.41 (1H, ddd, *J* 6.4, 6.4, 1.6); d_C (125 MHz) 193.6 (C=O), 148.2 (C), 133.5 (CH), 129.1 (C), 127.3 (CH), 125.6 (CH) and 124.6 (CH). Good agreement with the literature [8].

2-Mercaptobenzoyl chloride **1:** d_H (400 MHz) 8.33 (1H, ddd, *J* 8.0, 1.6, 0.4), 7.92 (1H, ddd, *J* 8.0, 1.0, 0.4), 7.76 (1H, ddd, *J* 8.4, 7.6, 1.6) and 7.42 (1H, ddd, *J* 8.4, 7.6, 1.0); d_C (125 MHz) 169.5 (C=O), 146.0 (C), 135.8 (CH), 134.6 (CH), 127.3 (C), 125.8 (CH) and 124.4 (CH). HSQC showed the following correlations: 8.33—134.6; 7.92–124.4; 7.76–135.8; 7.42–125.8. HRMS (ESI$^+$): found 170.9666. C_7H_4ClOS (M–H) requires 170.9671.

Prior to distillation, additional signals were present in both the ^{1}H and ^{13}C NMR spectra, indicating the presence of 2,2′-dithiodibenzoyl chloride **3** [6,7].

3.2. Formation and X-ray Structure Determination of 2,2′-Trisulfanediyldibenzoyl Chloride 5

Thiosalicylic acid (2-mercaptobenzoic acid) was added under a nitrogen atmosphere to hot thionyl chloride (5 mL), until no more dissolved. The solution was cooled to room temperature and filtered quickly under vacuum through a sintered glass funnel, then placed in a freezer at –30 °C. A crystal selected from the resulting solid was suitable for X-ray diffraction. The structure was determined using a Rigaku XtalLAB P200 diffractometer, using graphite monochromated Mo Kα radiation λ = 0.71073 Å.

Crystal data for $C_{14}H_8Cl_2O_2S_3$, M = 375.30 g mol^{-1}, colourless plate, crystal dimensions 0.12 × 0.02 × 0.01 mm, orthorhombic, space group Fdd2 (No. 43), a = 15.1011(10), b = 48.312(3), c = 4.2805(4) Å, V = 3122.9(4) Å^3, Z = 8, D_{calc} = 1.596 g cm^{-3}, T = 93 K, $R1$ = 0.0281, $Rw2$ = 0.0705 for 1475 reflections with $I > 2\sigma(I)$, and 96 variables, R_{int} 0.0611, goodness of fit on F^2 0.924. Data have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2240737. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/getstructures. The structure was solved using direct methods and refined by full-matrix least-squares against F^2 (SHELXL Version 2018/3 [22]).

Supplementary Materials: The following are available online, the ^{1}H, ^{13}C, and HSQC NMR spectra of **1**, and cif and check-cif files for **5**.

Author Contributions: A.H.C. and C.E.F. prepared the compounds, A.M.Z.S. collected the X-ray data and solved the structure; R.A.A. designed the study, analysed the data, and wrote the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The X-ray data are available at CCDC, as stated in the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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