

Structure of 4-Phenylthiazole-2(3*H*)-thione (1) and Bis(4-chlorophenacyl) Disulfide (2), the Product Obtained on its Gas–Solid Chlorination

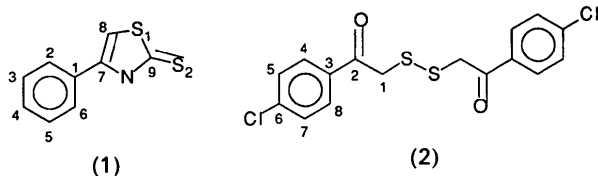
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Abstract. (1) $C_9H_7NS_2$, $M_r = 193$, monoclinic, $P2_1/n$, $a = 6.225$ (1), $b = 11.570$ (4), $c = 12.753$ (4) Å, $\beta = 101.68$ (3)°, $V = 899.5$ (8) Å³, $Z = 4$, $D_x = 1.42$, D_m (by flotation in benzene–carbon tetrachloride) = 1.42 (2) g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 47.9$ cm⁻¹, $F(000) = 400$, $T = 298$ K, $R = 0.046$, $wR = 0.064$ with 1484 independent observed reflections. (2) $C_{16}H_{12}Cl_2O_2S_2$, $M_r = 370$, monoclinic, $C2$, $a = 30.952$ (6), $b = 5.017$ (1), $c = 5.337$ (1) Å, $\beta = 90.67$ (3)°, $V = 828.7$ (8) Å³, $Z = 2$, $D_x = 1.48$, D_m (by flotation in benzene–carbon tetrachloride) = 1.44 (3) g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 57.12$ cm⁻¹, $F(000) = 380$, $T = 298$ K, $R = 0.071$, $wR = 0.067$ with 834 independent observed reflections. Crystalline thione (1) is converted to disulfide (2) by a crystal-structure-controlled chlorination–oxidation reaction characterized by some degree of topotaxy. The sheet structure of thione (1) helps in rationalizing a mechanism for solid-state chlorination.

Introduction. Crystal packing plays an important role in determining the vulnerability of an organic solid to gaseous reagents. In those cases where a gas–solid reaction is possible, the packing may also control product specificity (Paul & Curtin, 1975; Perrin, Lamartine, Perrin & Thozet, 1987). We observed that 4-phenylthiazole-2(3*H*)-thione, (1), crystallizes in yellow and white modifications, (1-Y) from ethyl acetate and (1-W) from benzene, respectively. When crystals of (1-W) were kept in an atmosphere of moist chlorine for several weeks at ambient temperatures, they were completely transformed into two products with no traces of the starting material (Nalini & Desiraju, 1987).



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The major product was identified spectroscopically as bis(4-chlorophenacyl) disulfide, (2). The minor product remains unidentified. Interestingly, crystals of (1-Y) were unreactive on treatment with moist chlorine and a crystallographic investigation on (1-W) and (1-Y) was therefore initiated. Since the formation of (2) in the gas–solid reaction was unexpected, its structure assignment was confirmed by an X-ray analysis of the recrystallized material. This paper presents the results of these three crystal-structure determinations. Crystals of reacted (1-W) also showed faint diffraction patterns but the high mosaicity of these crystals precluded any attempts at data collection.

Experimental. Intensity data on (1-W) and (1-Y) were collected and the structures solved by direct methods and refined routinely. Examination of the final coordinates of (1-W) and (1-Y) showed that these values were well within three e.s.d.'s of each other. No solvent molecules were present in either structure and no other unusual differentiating feature could be found. It was concluded therefore that (1-W) and (1-Y) are crystallographically identical. In the interest of brevity, the following section deals with the details of the structure determination of (1-W), the 'reactive' crystal.

Thione (1-W). Colourless well formed tablet 0.5 × 0.6 × 1.0 mm from benzene, Enraf–Nonius CAD-4 diffractometer. Unit-cell parameters were obtained from 25 reflections in the range 20 ≤ 2θ ≤ 26°. No absorption corrections, 2179 independent reflections, -7 ≤ h ≤ 7, 0 ≤ k ≤ 14, 0 ≤ l ≤ 16, 1484 non-zero with $I_o > 3.0\sigma(I_o)$, $[(\sin\theta)/\lambda]_{\max} = 0.63$ Å⁻¹, structure solution by direct methods using the program MULTAN80 (Main *et al.*, 1980), full-matrix least-squares refinement on F_o using the program SHELX76 (Sheldrick, 1976), isotropic refinement on H atoms and anisotropic refinement for non-H atoms, 138 parameters, converged at $R = 0.046$, $wR = 0.064$. The weights in the refinement were taken as $3.36/[\{\sigma(F_o)\}^2 + (0.03F_o)^2]$, $(\Delta/\sigma)_{\max} = 0.02$, maximum and minimum peaks in the final Fourier map 0.38 and -0.37 e Å⁻³, scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. Atomic coordinates and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

	$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$			$U_{eq}(\text{\AA}^2)$
	<i>x</i>	<i>y</i>	<i>z</i>	
(a) Thione (1)				
C(1)	0-1505 (5)	0-3003 (3)	-0-0253 (2)	0-035 (1)
C(2)	-0-0189 (6)	0-2200 (3)	-0-0484 (4)	0-044 (2)
C(3)	-0-2089 (6)	0-2466 (4)	-0-1221 (3)	0-056 (2)
C(4)	-0-2306 (6)	0-3526 (4)	-0-1723 (3)	0-059 (2)
C(5)	-0-0633 (7)	0-4334 (3)	-0-1483 (3)	0-055 (2)
C(6)	0-1257 (6)	0-4073 (3)	-0-0762 (3)	0-043 (2)
C(7)	0-3543 (5)	0-2721 (3)	0-0509 (2)	0-033 (1)
C(8)	0-4848 (6)	0-3417 (3)	0-1215 (3)	0-038 (2)
C(9)	0-6249 (5)	0-1416 (3)	0-1239 (2)	0-032 (1)
N(1)	0-4370 (4)	0-1607 (2)	0-0553 (2)	0-032 (1)
S(1)	0-7069 (1)	0-26783 (7)	0-19206 (7)	0-0397 (4)
S(2)	0-7640 (2)	0-01612 (7)	0-14226 (7)	0-0402 (4)
(b) Disulfide (2)				
C(1)	0-0473 (3)	0-703	-0-220 (1)	0-057 (4)
C(2)	0-0870 (2)	0-646 (2)	-0-058 (1)	0-054 (4)
C(3)	0-1181 (2)	0-445 (2)	-0-149 (1)	0-049 (3)
C(4)	0-1122 (2)	0-297 (2)	-0-364 (1)	0-053 (4)
C(5)	0-1418 (2)	0-112 (2)	-0-438 (1)	0-053 (4)
C(6)	0-1784 (2)	0-074 (2)	-0-297 (2)	0-059 (4)
C(7)	0-1862 (3)	0-214 (2)	-0-086 (2)	0-070 (5)
C(8)	0-1555 (2)	0-404 (2)	-0-009 (2)	0-064 (4)
O(1)	0-0910 (2)	0-760 (2)	0-140 (1)	0-081 (4)
S(1)	0-00675 (5)	0-4476 (6)	-0-1854 (3)	0-0501 (7)
Cl(1)	0-21641 (7)	-0-1555 (7)	-0-3969 (5)	0-0797 (3)

Table 2. Selected intramolecular bond lengths (\AA) and angles ($^\circ$); *e.s.d.*'s are in parentheses

(a) Thione (1)			
C(1)—C(2)	1-392 (5)	C(2)—C(3)	1-388 (6)
C(3)—C(4)	1-377 (6)	C(4)—C(5)	1-387 (6)
C(1)—C(6)	1-392 (5)	C(5)—C(6)	1-372 (6)
C(1)—C(7)	1-470 (4)	C(7)—C(8)	1-350 (5)
C(8)—S(1)	1-717 (2)	S(1)—C(9)	1-723 (1)
C(9)—S(2)	1-683 (1)	C(9)—N(1)	1-329 (4)
C(7)—N(1)	1-385 (4)		
(b) Disulfide (2)			
C(2)—C(1)—C(6)	119-2 (2)	C(2)—C(1)—C(7)	120-5 (2)
C(6)—C(1)—C(7)	120-3 (2)	C(1)—C(2)—C(3)	120-1 (2)
C(2)—C(3)—C(4)	120-1 (3)	C(4)—C(5)—C(6)	120-2 (3)
C(3)—C(4)—C(5)	119-9 (3)	C(1)—C(6)—C(5)	120-5 (3)
C(1)—C(7)—C(8)	129-1 (3)	C(1)—C(7)—N(1)	119-8 (2)
C(8)—C(7)—N(1)	111-1 (3)	C(7)—C(8)—S(1)	111-4 (1)
N(1)—C(9)—S(1)	108-8 (1)	N(1)—C(9)—S(2)	126-5 (1)
S(1)—C(9)—S(2)	124-7 (1)	C(8)—S(1)—C(9)	91-9 (1)
C(7)—N(1)—C(9)	116-8 (3)		
(b) Disulfide (2)			
C(1)—C(2)	1-522 (1)	C(2)—C(3)	1-480 (1)
C(3)—C(4)	1-377 (1)	C(4)—C(5)	1-366 (1)
C(1)—S(1)	1-805 (1)	C(5)—C(6)	1-365 (1)
C(6)—C(7)	1-347 (2)	C(7)—C(8)	1-410 (1)
C(3)—C(8)	1-386 (1)	C(6)—Cl(1)	1-735 (1)
C(2)—O(1)	1-207 (2)		
C(1)—C(2)—O(1)	117-5 (3)	C(3)—C(2)—O(1)	122-9 (3)
C(2)—C(3)—C(8)	117-8 (6)	C(1)—C(2)—C(3)	117-6 (6)
C(2)—C(3)—C(4)	124-1 (6)	C(4)—C(5)—C(6)	119-2 (5)
C(3)—C(4)—C(5)	121-6 (7)	C(4)—C(3)—C(8)	118-1 (6)
C(5)—C(6)—C(7)	122-1 (9)	C(5)—C(6)—Cl(1)	118-8 (1)
C(7)—C(6)—Cl(1)	119-1 (1)	C(6)—C(7)—C(8)	118-7 (6)
C(7)—C(8)—C(3)	120-3 (6)	C(1)—S(1)—S(1)	104-6 (1)

Disulfide (2). Colourless flake $0.3 \times 0.1 \times 0.5$ mm from acetone, Enraf-Nonius CAD-4 diffractometer. Unit-cell parameters were obtained from 25 reflections in the range $20 \leq 2\theta \leq 26^\circ$. No absorption corrections, 937 independent reflections, 834 non-zero with $I_o > 2.0\sigma(I_o)$, structure solution by direct methods using the program *MULTAN80* (Main *et al.*, 1980), full-matrix least-squares refinement on F_o using the program *SHELX76* (Sheldrick, 1976), isotropic refinement on H atoms and anisotropic refinement for non-H atoms, 101 parameters, converged at $R = 0.071$, $wR = 0.067$. The weights in the refinement were taken as $3.043/[\sigma(F_o)]^2 + (0.02F_o)^2$, $(\Delta/\sigma)_{\max} = 0.021$, maximum and minimum peaks in the final Fourier map 0.82 and $-0.41 e \text{\AA}^{-3}$, scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. *Thione* (1-W). Atomic coordinates are given in Table 1(a)* and bond lengths and angles in Table 2(a). The molecule clearly exists as the thione tautomer. The tautomeric preference of the compound is discussed in the following paper (Nalini & Desiraju, 1989). The molecule is significantly non-planar and the phenyl and heterocyclic rings make

an angle of $35.2 (1)^\circ$. Centrosymmetric molecules are $N-H \cdots S=C$ hydrogen bonded in a manner characteristic of thioamides [$N \cdots S$ is $3.29 (1) \text{\AA}$, the $N-H \cdots S$ angle is $169 (5)^\circ$]. Dimer pairs are arranged along the *a* axis to generate layers parallel to (001). There is a well defined interlamellar region which presumably permits easy entry of the gaseous reagents chlorine and water (Fig. 1).

Disulfide (2). Atomic coordinates are in Table 1(b) and bond lengths and angles in Table 2(b). The molecule lies on a twofold axis and the angle between the phenyl rings is $90.7 (2)^\circ$. A drawing of the structure down [010] is shown in Fig. 2. The molecules are held together by strong and directionally specific $S \cdots S$ contacts of $3.39 (2) \text{\AA}$. The geometry of these contacts is in accord with the electrophile-nucleophile model proposed by Parthasarathy (Row & Parthasarathy, 1981). There are also $C-H \cdots O$ contacts between H(5) of the reference molecule and carbonyl oxygen O(1) of the molecule at $x, 1+y, 1+z$ [$C \cdots O$ $3.25 (2) \text{\AA}$]. There is short $Cl \cdots Cl$ contact of $3.45 (2) \text{\AA}$ between twofold-axis-related molecules.

Relationship of these structures to the gas-solid reaction (1) \rightarrow (2). Two distinct solid-state reactions, namely an electrophilic chlorination and a heterocyclic ring oxidation, must take place in the conver-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51894 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

sion of (1) to (2). The former reaction probably proceeds by an addition-elimination mechanism as reported for crystalline chloro- and methylphenols (Lamartine, Perrin, Bertholon & Vincent-Falquet, 1977). In thione (1) the *para* position in the benzene ring is adjacent to the interlamellar region and is quite accessible to electrophilic attack by chlorine when compared to the two *ortho* positions. So, electronic factors apart, there is a good topochemical reason for the formation of the *para*-chloro derivative which is indeed the sole substitution product.

Like the *para*-C atoms, the heterocyclic S atoms adjoin the interlamellar region and should be amenable to oxidation by chlorine. Bonding between two such S atoms is necessary to form disulfide (2) and probably accompanies such an oxidation reaction. The nearest such S...S approach in crystalline (1) is across a distance of 5.96 (1) Å between screw-axis-related neighbours and it is perhaps not a coincidence that the disulfide bond in the product (2) is bisected by a crystallographic twofold axis. In fact, crystals of reacted (1) could be mounted and showed faint diffraction patterns indicating a partial

retention of single-crystal character. This probably shows that major molecular movements are unlikely in the coupling of two thione molecules to give a molecule of disulfide. Of course, the conformation of (2) in the present crystal structure need not be the same as that obtained in the solid-state reaction. There are examples where different conformations are obtained in the solid-state reaction and when the solid-state product is subsequently recrystallized from solvent (Nakanishi, Jones, Thomas, Hursthouse & Motevalli, 1981). Other mechanistic details of the heterocyclic ring oxidation have been published previously (Nalini & Desiraju, 1987).

It is unclear as to why the seemingly identical (1-W) and (1-Y) crystals differ in their behaviour towards chlorine. The stability of (1-Y) crystals may arise because some impurity in the solvent of crystallization is present in the crystal and blocks the entry of gaseous reagents. However, there is no spectroscopic evidence for the inclusion of any impurity. There is some similarity between this behaviour and observations recorded on crystals on calix(4)arene (Ungaro, Pochini, Andreetti & Sangermano, 1984).

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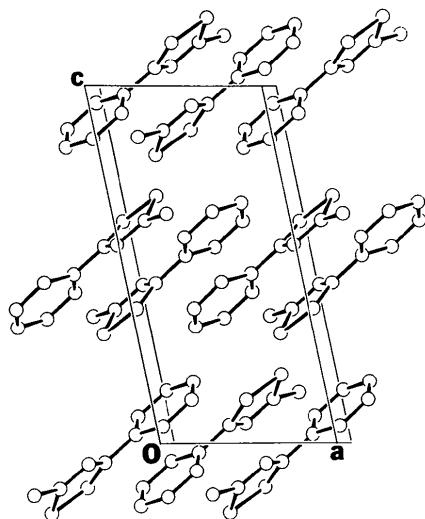


Fig. 1. View of the crystal structure of thione (1) down [010].

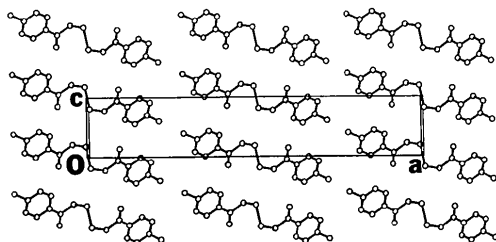


Fig. 2. View of the crystal structure of disulfide (2) down [010].