

## Tautomerism in Thiazolethiones. Structure of 4-(3-Nitrophenyl)thiazole-2(3H)-thione

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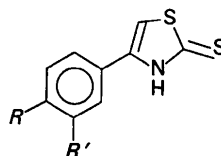
**Abstract.**  $C_9H_6N_2O_2S_2$ ,  $M_r = 238$ , monoclinic,  $P2_1/c$ ,  $a = 13.543$  (2),  $b = 19.201$  (3),  $c = 7.279$  (2) Å,  $\beta = 148.77$  (5)°,  $V = 981.4$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.59$ ,  $D_m$  (by flotation in benzene-carbon tetrachloride) =  $1.64$  (2) g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54184$  Å,  $\mu = 4.5$  cm<sup>-1</sup>,  $F(000) = 488$ ,  $T = 298$  K,  $R = 0.053$ ,  $wR = 0.060$  for 1245 independent observed reflections. X-ray analysis establishes that the molecule exists in the solid state as the thione tautomer; this tautomeric preference is also paralleled in two related thiones [Nalini & Desiraju (1987). *Tetrahedron*, **43**, 1313–1320; Nalini & Desiraju (1989). *Acta Cryst.* **C45**, 1525–1527]. The heterocyclic C—N and C—S bonds are 1.357 (6) and 1.712 (1) Å while the exocyclic C=S bond is 1.685 (1) Å. The angle between the phenyl and heterocyclic rings is 3.9 (2)° and the angle between the phenyl ring and the nitro group is 10.4 (2)°.

**Introduction.** While several spectroscopic methods may be used to ascertain the tautomeric preference of substituted heterocyclic compounds in the solid state, X-ray crystallography remains the most direct means of obtaining information on bond lengths and angles and, in favourable cases, on H-atom positions. Such information is often used to resolve tautomeric questions unambiguously (Elguero, Marzin, Linda & Katritzky, 1976).



Tautomerism in the family of substituted thiazole-2(3H)-thiones has been reviewed (Metzger, 1979). The thione form generally predominates and the only evidence for the thiol form arises from some infrared and other spectroscopic studies (Chanon & Metzger, 1968; Stern, 1949). Theoretical work has also indicated the stability of the thione form (Bouscasse, Chanon, Phan Tan Luu, Vincent & Metzger, 1972; Kjellin & Sandstrom, 1969). The behaviour of the

4-phenyl derivative has been the subject of several studies (Metzger, 1979; Chanon & Metzger, 1968; Selim & Selim, 1969; Ellis & Griffiths, 1966). In the course of our own work on the solid-state chemistry of these compounds, we have prepared compounds (1)–(3).



- (1)  $R = R' = \text{H}$   
 (2)  $R = \text{Cl}; R' = \text{H}$   
 (3)  $R = \text{H}; R' = \text{NO}_2$

The unsubstituted phenyl thione (1) may be chlorinated topochemically (Nalini & Desiraju, 1987a, 1989) while the (chlorophenyl) thione (2) is extremely photoreactive, participating in an olefin metathesis reaction (Nalini & Desiraju, 1986, 1987b). Crystallographic investigations on both compounds (1) and (2) have shown the presence of the thione tautomer exclusively (Nalini & Desiraju, 1987b, 1989). Further, crystals of compound (2) consist of two symmetry-independent molecules, but both exist as the thione tautomer. In this paper, we report the crystal structure of the nitro derivative (3) and comment on the tautomeric preferences in all three crystal structures.

**Experimental.** Thione (3) was prepared by adding 18 g of 3-nitrophenacyl bromide, obtained from 3-nitroacetophenone by reported procedures (Blatt, 1943), to a solution of freshly prepared ammonium dithiocarbonate (Audrieth, 1980) in ethanol (14 g in 300 ml). The mixture was refluxed for 3 h, well shielded from light. Solid  $\text{NH}_4\text{Br}$  separated out at the end of the reaction and was filtered off. Most of the solvent was removed under reduced pressure and the residue recrystallized several times from acetone to leave the pure thione. Yield 10.5 g (53%), m.p. 517–518 K, IR (KBr)  $\nu_{\text{max}}$  (cm<sup>-1</sup>) 3100 (N—H), 1520 (N—O asym.), 1360 (N—O sym.), 1080 (C=S), 850 (C—N); <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>)  $\delta$  3.5–3.8 (*s*, 1H), 7.6 (*s*, 1H), 7.7–8.4 (*m*, 4H); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>)  $\delta$  120.5, 132.8, 133.9, 134.2, 135.6, 137.6, 139.7, 143.9, 197.9 (C=S). Crystals suitable for X-ray diffraction

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Table 1. Atomic coordinates and equivalent isotropic thermal parameters for thione (3) with e.s.d.'s in parentheses

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(1)	0.5608 (5)	1.0941 (2)	0.4423 (9)	0.0288 (21)
C(2)	0.7545 (5)	1.1063 (2)	0.7832 (9)	0.0306 (22)
C(3)	0.8113 (5)	1.1714 (2)	0.9353 (9)	0.0264 (21)
C(4)	0.6858 (5)	1.2260 (2)	0.7685 (10)	0.0355 (23)
C(5)	0.4947 (6)	1.2135 (2)	0.4321 (10)	0.0366 (24)
C(6)	0.4331 (5)	1.1488 (2)	0.2709 (10)	0.0297 (22)
C(7)	0.4995 (5)	1.0246 (2)	0.2767 (9)	0.0276 (20)
C(8)	0.6099 (6)	0.9692 (2)	0.4050 (10)	0.0323 (22)
C(9)	0.2695 (6)	0.9461 (1)	-0.1930 (10)	0.0364 (23)
N(1)	0.3091 (5)	1.0095 (2)	-0.0570 (8)	0.0301 (19)
N(2)	1.0156 (5)	1.1835 (2)	1.2929 (8)	0.0361 (21)
O(1)	1.1285 (5)	1.1382 (2)	1.4183 (8)	0.0439 (19)
O(2)	1.0637 (4)	1.2373 (2)	1.4503 (8)	0.0439 (19)
S(1)	0.4770 (1)	0.90042 (5)	0.1104 (2)	0.0338 (7)
S(2)	0.0548 (2)	0.91548 (6)	-0.5994 (3)	0.0369 (7)

were obtained by careful recrystallization from 10:1 ethyl acetate-acetone. Slow evaporation of the solvent gave hexagonal-shaped yellow tablets.

Intensity data were collected on a well formed crystal  $0.35 \times 0.21 \times 0.06$  mm on a Syntex  $P2_1$  diffractometer. Unit-cell parameters were obtained from 25 reflections in the range  $20 \leq 2\theta \leq 26^\circ$ . No absorption corrections, 1757 independent reflections,  $14 \leq h \leq 0$ ,  $0 \leq k \leq 20$ ,  $-7 \leq l \leq 7$ , 1245 non-zero with  $I > 2.0\sigma(I)$ , three standard reflections  $1\bar{3}1$ ,  $\bar{1}11$  and 100 measured every 60 reflections showed less than 1% variation,  $[(\sin\theta)/\lambda]_{\max} = 0.538 \text{ \AA}^{-1}$ , structure solution by direct methods using the program *SHELXS86* (Sheldrick, 1985), 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 converged at  $R = 0.053$ ,  $wR = 0.060$ . The weights in the refinement were taken as  $9.2496/[\sigma(F_o)^2 + (0.02F_o)^2]$ ,  $(\Delta/\sigma)_{\max} = 0.032$ , maximum and minimum peaks in the final Fourier map  $0.34$  and  $-0.35 \text{ e \AA}^{-3}$ , scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** Atomic positions and equivalent isotropic temperature factors are listed in Table 1.\* The bond lengths and angles for (3) are given in Table 2 and the atom-numbering scheme is given in Fig. 1. The molecule clearly exists as the thione tautomer with C(9)—S(2) being  $1.685(1) \text{ \AA}$  and C(9)—N(1)  $1.357(6) \text{ \AA}$ . Further, the tautomeric H was unambiguously revealed in the Fourier map and refined

\* 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 51895 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Intramolecular bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for thione (3) with some comparison values for thiones (1) and (2) and some details of N—H...S—C hydrogen-bond geometry in the three thiones

	E.s.d.'s are in parentheses.			
	(3)	(1)	(2A)	(2B)
<b>(a) Bond lengths</b>				
C(7)—N(1)	1.386 (9)	1.385 (4)	1.384 (4)	1.368 (6)
C(7)—C(8)	1.361 (8)	1.350 (5)	1.380 (2)	1.334 (4)
C(8)—S(1)	1.727 (1)	1.717 (2)	1.729 (1)	1.746 (2)
C(9)—S(1)	1.712 (1)	1.723 (1)	1.743 (1)	1.736 (1)
C(9)—S(2)	1.685 (1)	1.683 (1)	1.661 (1)	1.657 (2)
C(9)—N(1)	1.357 (6)	1.329 (4)	1.338 (4)	1.351 (6)
C(1)—C(2)	1.401 (9)			
C(2)—C(3)	1.387 (6)			
C(3)—C(4)	1.390 (8)			
C(4)—C(5)	1.383 (8)			
C(5)—C(6)	1.394 (7)			
C(1)—C(6)	1.399 (8)			
C(1)—C(7)	1.487 (8)			
C(3)—N(2)	1.472 (9)			
N(2)—O(1)	1.241 (7)			
N(2)—O(2)	1.236 (6)			
<b>(b) Bond angles</b>				
C(8)—S(1)—C(9)	91.6 (4)	91.9 (1)	92.7 (6)	91.6 (6)
C(8)—C(7)—N(1)	110.2 (6)	111.1 (3)	112.5 (7)	115.0 (9)
C(7)—C(8)—S(1)	112.3 (3)	111.4 (1)	109.6 (5)	109.5 (5)
N(1)—C(9)—S(1)	109.3 (5)	108.8 (1)	108.6 (5)	109.2 (6)
N(1)—C(9)—S(2)	127.3 (4)	126.5 (1)	128.4 (4)	127.7 (5)
S(1)—C(9)—S(2)	123.4 (4)	124.7 (1)	123.0 (3)	123.1 (4)
C(7)—N(1)—C(9)	116.6 (4)	116.8 (3)	116.6 (6)	114.7 (9)
C(1)—C(2)—C(6)	118.0 (5)			
C(2)—C(1)—C(7)	119.2 (3)			
C(6)—C(1)—C(7)	122.8 (6)			
C(1)—C(2)—C(3)	119.0 (3)			
C(2)—C(3)—C(4)	123.6 (5)			
C(4)—C(3)—N(2)	118.1 (4)			
C(3)—C(4)—C(5)	117.1 (6)			
C(4)—C(5)—C(6)	120.8 (5)			
C(1)—C(6)—C(5)	121.6 (6)			
C(1)—C(7)—C(8)	128.4 (6)			
C(1)—C(7)—N(1)	121.4 (5)			
C(3)—N(2)—O(1)	117.4 (5)			
C(3)—N(2)—O(2)	118.3 (4)			
O(1)—N(2)—O(2)	124.2 (5)			
<b>(c) Hydrogen-bond geometry</b>				
	N...S	N—H	N—H...S	
	( $\text{\AA}$ )	( $\text{\AA}$ )	(°)	
(1)	3.29 (1)	0.78 (3)	169 (5)	
(2A)	3.29 (1)	1.11 (4)	167 (5)	
(2B)	3.33 (1)	1.06 (4)	167 (6)	
(3)	3.39 (1)	0.82 (4)	149 (6)	

without problems to an N—H distance of  $0.82(4) \text{ \AA}$ . Centrosymmetric molecules are N—H...S=C hydrogen bonded in a manner characteristic of thioamides [N...S is  $3.39(1) \text{ \AA}$ ]. This behaviour is reminiscent of '2-aminobenzothiazole' which actually exists as the thione (Chesick & Donohue, 1971) and is also seen in the related thiones (1) and (2) (Nalini & Desiraju, 1986, 1989). The packing of the molecules is shown in Fig. 2. Hydrogen-bonded dimers are packed so as to optimize S...O [ $3.09(1) \text{ \AA}$ ] and C—H...O [ $2.83(7) \text{ \AA}$ ] interactions between the nitro groups of the reference molecule and heterocyclic S and aromatic H atoms of the glide-related molecules.

An examination of bond lengths and angles in the heterocyclic rings of thiones (1), (2) and (3) shows that these are very similar indeed in all three cases, being within three e.s.d.'s of one another. Table 2 contains pertinent data and reveals the close tautomeric relationships between these compounds. Such comparisons are valid because early work (Wheatley, 1961) shows that the bond lengths and angles should be significantly different in the thiol tautomer. In all three thiones, the molecules exhibit  $N-H\cdots S=C$  hydrogen bonds across centres of inversion. The  $N\cdots S$  distances are comparable as are the  $N(1)-C(9)-S(2)$  angles. There is some inevitable scatter in the bond lengths and angles involving the tautomeric H for the three structures; this is probably due to limitations in the data and refinement and one may conclude that the tautomeric H atom is definitely attached to N rather than to S in all three compounds.

It is pertinent to comment here on the adoption of a centrosymmetric space group by the title compound. Currently there is much interest in 'engineering' the crystal structure of an organic compound into a non-centrosymmetric space group for possible applications in non-linear optics (Williams, 1983). An empirical rule in this context is that *meta*-disubstituted benzenes, especially nitrobenzenes, are

more likely to adopt non-centrosymmetric space groups than are the corresponding *ortho* and *meta* derivatives (Curtin & Paul, 1981; Desiraju & Krishna, 1988). Thione (3) does happen to be a *meta*-substituted nitrobenzene. However, the presence of the secondary thioamide  $NH-C=S$  linkage in the molecule strongly influences the packing motif; the formation of inversion-related hydrogen-bonded dimer pairs leads naturally to the adoption of a centrosymmetric space group, overriding any other seeming preference for a non-centrosymmetric space group.

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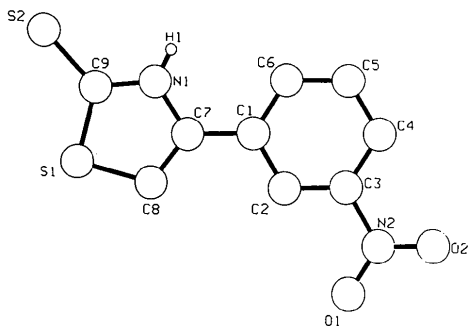


Fig. 1. Atom-numbering scheme in the title molecule.

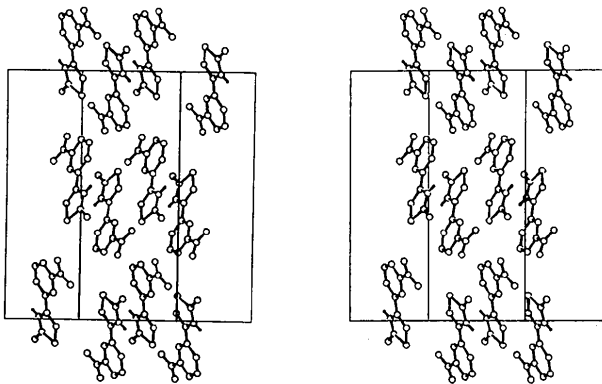


Fig. 2. Stereodrawing of the crystal structure of thione (3) down [001].