Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# *N*-(3*H*-Thiazol-2-ylidene)nitramine and *N*-methyl-*N*-(thiazol-2-yl)nitramine

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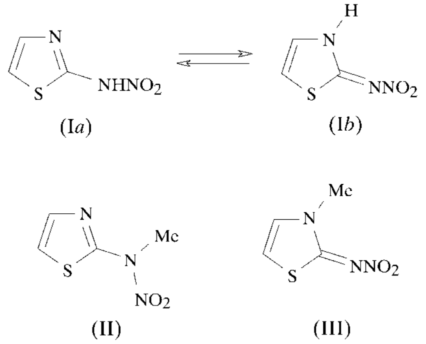
Received 22 December 2003
Accepted 20 January 2004

The geometries of the thiazole ring and the nitramino groups in *N*-(3*H*-thiazol-2-ylidene)nitramine, $C_3H_3N_3O_2S$, (I), and *N*-methyl-*N*-(thiazol-2-yl)nitramine, $C_4H_5N_3O_2S$, (II), are very similar. The nitramine group in (II) is planar and twisted along the C—N bond with respect to the thiazole ring. In both structures, the asymmetric unit includes two practically equal molecules. In (I), the molecules are arranged in layers connected to each other by N—H···N and much weaker C—H···O hydrogen bonds. In the crystal structure of (II), the molecules are arranged in layers bound to each other by both weak C—H···O hydrogen bonds and S···O dipolar interactions.

## Comment

Primary nitramines display acidic properties, *e.g.* the p$K_a$ values of ring-substituted *N*-phenylnitramines vary from 3.77 to 5.62, depending on the electronic character of the substituent (Daszkiewicz, Spaleniak & Kyzioł, 2002). *N*-(4-Pyridyl)nitramine is much less acidic (p$K_a$ = 8.01), probably as a result of tautomerism; in the crystalline lattice it exists in the nitrimine form, *i.e.* as 1,4-dihydro-4-nitriminopyridine (Krygowski *et al.*, 1996). IR spectroscopy indicates that the nitrimine form also prevails in solution (Kyzioł *et al.*, 2002). The molecule of *N*-(thiazol-2-ylidene)nitramine, (I), also contains acidic ($NHNO_2$) and basic (—N=) centers and hence analogous tautomerism cannot be excluded. However, the acidity (p$K_a$ = 4.00) is similar to that of typical primary nitramines.



Within the pyridine series, we have observed some differences in the geometry of the ring and the $NNO_2$ group between nitramine and isomeric nitrimine (Kyzioł *et al.*, 2002). In the present paper, we establish the structure of *N*-(thiazol-2-ylidene)nitramine to be (I*b*) (see scheme and Fig. 1*a*) and compare this structure with that of *N*-methyl-*N*-(thiazol-2-yl)nitramine, (II) (Fig. 1*b*), and its isomer 2,3-dihydro-3-methyl-2-nitriminothiazole, (III) (Kyzioł *et al.*, 2000).

The geometries of the thiazole rings and the nitramine groups in (I*b*) and (II) are very similar (Tables 1 and 3). The formally single C2—N3 bond in (I*b*) is only 0.03 Å longer than that in (II), while the C2—N6 bond is 0.05 Å shorter. Surprisingly, the N—N bond lengths are nearly the same in the two compounds. The mean N3—C2—S1 angle is greater in nitramine (II) [115.9 (1)°] than in nitrimine (I*b*) [110.6 (2)°]. Significant differences are also seen in the mean C2—N3—C4 angle, which is 109.3 (1)° in (II) and 114.9 (1)° in (I*b*), The geometry of the ring is typical of thiazole derivatives (*e.g.* Caranoni & Reboul, 1982).

The shapes of the $NNO_2$ groups are also very similar; the mean N—O bond lengths in (I*b*) and (II) are 1.243 (6) and 1.229 (2) Å, respectively. The results correspond well to the notation given on the scheme above.

The nitramine group in (II) is planar and twisted along the C2—N6 bond with respect to the thiazole ring; details of relevant torsion angles are given in Table 3. In other *N*-aryl-*N*-methylnitramines, the planes of the nitramine group and the thiazole ring are nearly perpendicular (Daszkiewicz, Zaleski *et al.*, 2002). Such a conformation probably results from the crystal packing since the rotational energy barrier (*ca* 12 kJ mol$^{-1}$) along the aryl–nitrogen bond is rather low. Spectral and chemical properties of thiazolylnitramines are very similar to phenyl- and pyridylnitramines, hence the

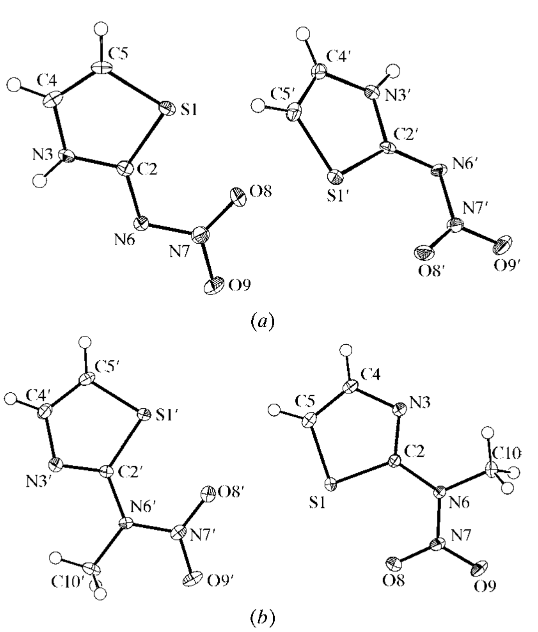


**Figure 1**
The molecular structures of (*a*) (I*b*) and (*b*) (II). Displacement ellipsoids are drawn at the 50% probability level.

DOI: 10.1107/S0108270104001428

mesomeric interaction between the nitramine group and the thiazole ring may be excluded.

Hydrogen bonding plays an important role in the crystal packing of (I*b*). In the IR spectrum (recorded as a KBr pellet), the hydrogen bonding is observed as an intense and broad band in the 3100–2626 $\text{cm}^{-1}$ region, with several submaxima. The band corresponding to the N—H stretching vibrations appears at 3604 $\text{cm}^{-1}$, when the spectrum is recorded in a dilute deuterochloroform solution.

Molecules of (I*b*) are linked by N—H···N and weak C—H···O hydrogen bonds (Table 2), forming layers in the *ac* plane (Fig. 2*a*). The shortest S···O separations are S1···O8′($x$, $2 - y$, $\frac{1}{2} + z$) of 3.219 (2) Å and S1′···O8 of 3.148 (2) Å.

Molecules of (II) are linked by weak C—H···O hydrogen bonds (Table 4), forming layers in the *ab* plane (Fig. 2*b*). Close intermolecular contacts are also found between S and O atoms [S1···O8′ = 3.145 (2) Å and S1′···O8($1 + x$, $y$, $z$) = 3.048 (2) Å], which are shorter than the sum of the van der Waals radii (3.25 Å; Pauling, 1960).

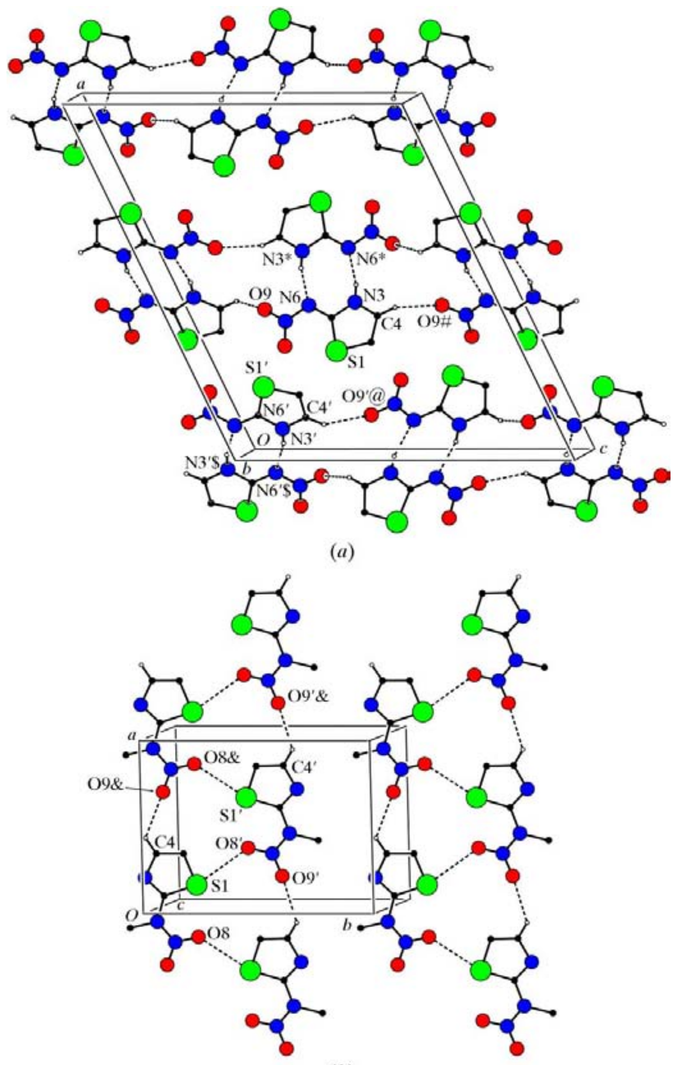


**Figure 2**

Packing diagrams of (*a*) (I*b*) and (*b*) (II), showing the hydrogen-bonding schemes. Atoms marked with an asterisk (*), hash (#), dollar sign ($), ‘at’ symbol (@) or ampersand (&) are at the symmetry positions. ($1 - x$, $1 - y$, $1 - z$), ($x$, $1 - y$, $\frac{1}{2} + z$), ($-x$, $-y$, $-z$), ($x$, $-y$, $\frac{1}{2} + z$) and ($1 + x$, $y$, $z$), respectively.

## Experimental

The preparation of (I*b*) by nitration of 2-aminothiazole in 77% sulfuric acid has been described previously by Kyzioł *et al.* (2000). Crystals were obtained by crystallization from nitromethane. Compound (II) was obtained according to the method of Angeli (Angeli & Valovi, 1912). A solution of 2-(*N*-methylamino)thiazole (2.30 g, 0.02 mol) and sodium hydride (1.60 g, 0.04 mol of 60% NaH) in boiling benzene (120 ml) was refluxed for 1 h under a dry nitrogen atmosphere. The mixture was cooled to room temperature and *n*-butyl nitrate (5.00 g, 0.04 mol) diluted with benzene (5 ml) was added. The brown solution was stirred for 1 h at room temperature, and then water (20 ml) and acetic acid (2 ml) were added and the layers separated. The benzene solution was extracted with sodium hydrogen sulfate (10% aqueous, 2 × 30 ml) and water, dried with anhydrous magnesium sulfate and evaporated in a vacuum. The residue was dissolved in *n*-hexane, stirred with charcoal, filtered and cooled in a dry-ice box. Compound (II) (1.75 g, 55%) was collected by filtration (m.p. 319–321 K). Low-temperature crystallization from *n*-hexane provided crystals suitable for X-ray diffraction studies. MS (*m*/*z*): 145 ($M^+$, 10), 113 (94), 86 (3), 69 (100), 59 (11), 58 (15), 42 (30), 30 (14); IR (KBr): 3130 (aromatic protons), 1537, 1272 (*N*-nitro group); $^1$H NMR (DMSO-$d_6$): $\delta$ 7.70 (*d*, 1H) and 7.59 (*d*, $^3J$ = 3.8 Hz, 1H, aromatic protons), 3.99 (*s*, 3H, *N*-methyl group); $^{13}$C NMR (DMSO-$d_6$): $\delta$ 157.8 (C–2), 138.7 (C–4), 118.2 (C–5), 37.3 (*N*-methyl group).

### Compound (I)

*Crystal data*

$C_3H_3N_3O_2S$
$M_r$ = 145.14
Monoclinic, $P2/c$
$a$ = 18.737 (3) Å
$b$ = 3.727 (1) Å
$c$ = 16.617 (2) Å
$\beta$ = 114.57 (2)°
$V$ = 1055.3 (4) Å$^3$
$Z$ = 8

$D_x$ = 1.827 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 2459 reflections
$\theta$ = 3.5–27.6°
$\mu$ = 0.53 mm$^{-1}$
$T$ = 100 (2) K
Irregular, white
0.3 × 0.3 × 0.2 mm

**Table 1**

Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| S1—C2 | 1.721 (2) | S1′—C2′ | 1.725 (2) |
| S1—C5 | 1.731 (2) | S1′—C5′ | 1.727 (2) |
| C2—N3 | 1.333 (2) | C2′—N3′ | 1.335 (2) |
| C2—N6 | 1.356 (2) | C2′—N6′ | 1.345 (2) |
| C4—C5 | 1.336 (3) | C4′—C5′ | 1.340 (3) |
| N6—N7 | 1.342 (2) | N6′—N7′ | 1.346 (2) |
| N7—O9 | 1.237 (2) | N7′—O9′ | 1.236 (2) |
| N7—O8 | 1.250 (2) | N7′—O8′ | 1.247 (2) |
| | | | |
| C2—S1—C5 | 90.28 (9) | C2′—S1′—C5′ | 90.47 (9) |
| N3—C2—N6 | 117.28 (17) | N3′—C2′—N6′ | 117.72 (16) |
| N3—C2—S1 | 110.84 (14) | N3′—C2′—S1′ | 110.44 (14) |
| N6—C2—S1 | 131.88 (15) | N6′—C2′—S1′ | 131.84 (14) |
| C2—N3—C4 | 114.80 (16) | C2′—N3′—C4′ | 115.08 (16) |
| N7—N6—C2 | 116.17 (15) | C2′—N6′—N7′ | 116.43 (15) |
| O9—N7—O8 | 123.05 (16) | O9′—N7′—O8′ | 123.03 (16) |
| O9—N7—N6 | 115.34 (16) | O9′—N7′—N6′ | 115.72 (16) |
| O8—N7—N6 | 121.61 (16) | O8′—N7′—N6′ | 121.24 (15) |
| | | | |
| N3—C2—N6—N7 | −179.69 (16) | N3′—C2′—N6′—N7′ | 177.19 (15) |
| S1—C2—N6—N7 | 1.5 (3) | S1′—C2′—N6′—N7′ | −3.7 (3) |

*Data collection*

Oxford Diffraction Xcalibur diffractometer
$\omega$ scans
7430 measured reflections
2740 independent reflections
1915 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\rm max} = 29.7°$
$h = -26 \rightarrow 23$
$k = -5 \rightarrow 3$
$l = -22 \rightarrow 23$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.093$
$S = 1.04$
2740 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.52$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.39$ e Å$^{-3}$

**Table 2**
Hydrogen-bonding geometry (Å, °) for (I).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3—H3···N6$^{\rm i}$ | 0.86 | 2.05 | 2.880 (2) | 163 |
| N3′—H3′···N6′$^{\rm ii}$ | 0.86 | 2.05 | 2.885 (2) | 163 |
| C4—H4···O9$^{\rm iii}$ | 0.93 | 2.54 | 3.276 (2) | 136 |
| C4′—H4′···O9′$^{\rm iv}$ | 0.93 | 2.59 | 3.360 (2) | 141 |

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $-x, -y, -z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $x, -y, \frac{1}{2}+z$.

## Compound (II)

*Crystal data*

$C_4H_5N_3O_2S$
$M_r = 159.17$
Monoclinic, $P2_1/c$
$a = 8.667$ (2) Å
$b = 11.473$ (2) Å
$c = 12.919$ (3) Å
$\beta = 96.80$ (3)°
$V = 1275.6$ (5) Å$^3$
$Z = 8$
$D_x = 1.658$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3361 reflections
$\theta = 2.4$–30.1°
$\mu = 0.44$ mm$^{-1}$
$T = 100$ (2) K
Irregular, white
0.25 × 0.20 × 0.20 mm

**Table 3**
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| S1—C2 | 1.7300 (18) | S1′—C2′ | 1.7280 (19) |
| S1—C5 | 1.7118 (19) | S1′—C5′ | 1.7182 (19) |
| C2—N3 | 1.302 (2) | C2′—N3′ | 1.299 (2) |
| C2—N6 | 1.400 (2) | C2′—N6′ | 1.404 (2) |
| N3—C4 | 1.377 (2) | N3′—C4′ | 1.377 (2) |
| C4—C5 | 1.351 (3) | C4′—C5′ | 1.349 (3) |
| N6—N7 | 1.350 (2) | N6′—N7′ | 1.353 (2) |
| N6—C10 | 1.461 (2) | N6′—C10′ | 1.462 (2) |
| N7—O9 | 1.227 (2) | N7′—O9′ | 1.226 (2) |
| N7—O8 | 1.229 (2) | N7′—O8′ | 1.232 (2) |
| | | | |
| C5—S1—C2 | 88.39 (9) | C5′—S1′—C2′ | 88.31 (9) |
| N3—C2—N6 | 119.05 (16) | N3′—C2′—N6′ | 118.50 (16) |
| N3—C2—S1 | 115.81 (13) | N3′—C2′—S1′ | 116.05 (13) |
| N6—C2—S1 | 125.09 (14) | N6′—C2′—S1′ | 125.45 (14) |
| C2—N3—C4 | 109.36 (16) | C2′—N3′—C4′ | 109.28 (16) |
| N7—N6—C2 | 120.60 (15) | N7′—N6′—C2′ | 120.92 (15) |
| N7—N6—C10 | 117.43 (15) | N7′—N6′—C10′ | 116.95 (15) |
| C2—N6—C10 | 121.83 (15) | C2′—N6′—C10′ | 121.79 (16) |
| O9—N7—O8 | 124.65 (16) | O9′—N7′—O8′ | 125.12 (17) |
| O9—N7—N6 | 117.29 (16) | O9′—N7′—N6′ | 117.14 (16) |
| O8—N7—N6 | 118.05 (15) | O8′—N7′—N6′ | 117.74 (15) |
| | | | |
| N3—C2—N6—N7 | −167.56 (16) | N3′—C2′—N6′—N7′ | 176.65 (16) |
| S1—C2—N6—N7 | 15.1 (2) | S1′—C2′—N6′—N7′ | −3.9 (2) |

**Table 4**
Hydrogen-bonding geometry (Å, °) for (II).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C4—H4···O9$^{\rm i}$ | 0.95 | 2.42 | 3.068 (2) | 125 |
| C4′—H4′···O9′$^{\rm i}$ | 0.95 | 2.43 | 3.094 (2) | 127 |

Symmetry code: (i) $1+x, y, z$.

*Data collection*

Oxford Diffraction Xcalibur diffractometer
$\omega$ scans
3561 measured reflections
3361 independent reflections
2340 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.010$
$\theta_{\rm max} = 30.1°$
$h = -12 \rightarrow 0$
$k = 0 \rightarrow 15$
$l = -18 \rightarrow 18$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.096$
$S = 1.06$
3361 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 0.7169P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.36$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.32$ e Å$^{-3}$

All H atoms were located from difference maps and subsequently treated as riding atoms, with C—H = 0.93–0.98 Å and N—H = 0.86 Å. $U_{\rm iso}$(H) values were set at $1.2U_{\rm eq}$(C or N), and $1.5U_{\rm eq}$(C) for the methyl H atoms.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1637). Services for accessing these data are described at the back of the journal.

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