2,3-Dihydro-3-methyl-2-nitrimino-1,3-thiazole

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The title compound {alternatively, 3-methyl-2-[oxido(oxo)hydrazono]-2,3-dihydro-1,3-thiazole}, $C_4H_5N_3O_2S$, was obtained by methylation of N-(2-thiazolyl)nitramine. The molecule lies on a mirror plane and the thiazole ring is planar, regular in shape and aromatic. The S atom participates in the aromatic sextet via an electron pair on the $3p_z$ orbital. In the crystal, the molecules are arranged in parallel layers, bound to each other by weak $C-H\cdots O$ and $C-H\cdots N$ hydrogen bonds and by $S\cdots O$ dipolar interactions, with an interlayer separation of 3.23 Å.

Comment

During nearly a hundred years of investigation into the mechanism of nitramine rearrangement, it has been established that the N-nitro group is shifted three or five nodes from the migration origin, the rearrangement is intramolecular and the susceptibility of an N-nitro compound to rearrangement is determined by the electronic properties of the migration terminus. It has been claimed that nitration of 5-nitroindazole provides 2,5-dinitroindazole, which rearranges at elevated temperature to 3,5-dinitroindazole (Cohen-Fernandes & Habraken, 1971). Our X-ray diffraction studies revealed that the substrate is, in fact, 1,5-dinitroindazole (Zaleski et al., 1998), hence the first of the above rules is obeyed in this case. The rearrangement of N-methyl-N-(2-thiazolyl)nitramine seems to infringe the remaining rules, so it requires special consideration. 2-Aminothiazole can be nitrated, under appropriate conditions, to N-(2-thiazolyl)nitramine, (I) (Kasman & Taurins, 1956). Its methylation provides another N-nitro compound, to which the structure of N-methyl-N-(2-thiazolyl)nitramine, (II), was assigned by Dickey et al. (1955). This compound (m.p. 542 K) was employed in investigations of the mechanism of nitramine rearrangement. The results were rather strange: the nitramine rearranged only in concentrated sulfuric acid and the nitro-group migration was intermolecular (Nemes & Tòth, 1975; Tòth et al., 1976; Tòth & Podányi, 1984). We have obtained N-methyl-N-(2-thiazolyl)nitramine (m.p. 319–321 K) by another route and

found that its properties are quite different from those of the aforementioned compound. In this work, we demonstrate that methylation of (I) gives 2,3-dihydro-3-methyl-2-nitriminothiazole, (III), and hence all Tòth's conclusions are invalid.
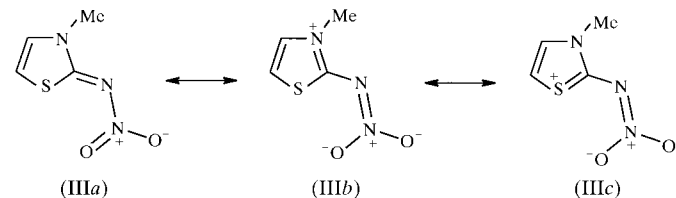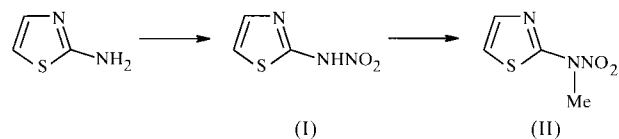
The molecular structure of (III) has some interesting features. The thiazole ring is planar, regular in shape and aromatic. The structures of aromatic nitrimines used to be represented by formulae analogous to (IIIa). However, all three $C-N$ bonds around N3 are coplanar, indicating trigonal hybridization of the ring nitrogen. The C2—N6 and C2—N3 bonds (Fig. 1) are of nearly the same length, hence they must be of the same bond order. The C4—N3 bond is 0.042 (2) Å longer than the C2—N3 bond; consequently, another mesomeric form, (IIIb), is a much better representation of the electronic structure of the nitrimine than (IIIa).

Both $C-S$ bonds are of identical length, within experimental error, and form an angle of nearly 90°. Such a geometry is characteristic of the thiazole ring (Caranoni & Reboul, 1982; Form et al., 1974) and indicates that S1 participates in the aromatic sextet with an electron pair on the $3p_z$ orbital. This mesomeric interaction is represented by the (IIIc) canonical form.

The nitrimino group in the molecule of (III) has a similar geometry to those we have observed in nitrimines of the pyridine series (Bujak et al., 1998; Daszkiewicz et al., 1999). The N—N bond is relatively short (1.33–1.34 Å) and the nitrimino group is bound to the ring with a $C-N$ bond of 1.366 (2) Å. The $C-N-N$ angle varies within the range 115–120°. Another common feature is the mean valence angle
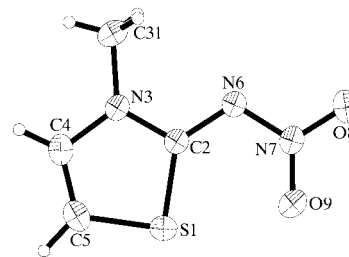

Figure 1
The molecular structure of (III), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

centred on C2, which is close to the theoretical value of 120°. The S1—C2—N6 angle is slightly greater [131.6 (1)°] than can be predicted from sp^2 hybridization, whereas N3—C2—N6 is slightly smaller [117.4 (1)°]. This is the result of the repulsion between S1 and O9.

It should be emphasized that the molecules of (III) are planar. An analogous conformation was observed in 1,2-dihydro-1-methyl-4-nitriminopyridine, (IV) (Bujak *et al.*, 1998), where the torsion angle along the C1—N2 bond did not exceed 8°. On the contrary, significant deformations were observed in the molecule of 1,2-dihydro-1-methyl-2-nitriminopyridine, (V) (Daszkiewicz *et al.*, 1999), where the nitrimino group was twisted by 28° from the ring plane and the torsion angle along the N—N bond was 18°. Considering the planar conformations of (III) and (IV), we can postulate that conjugation between the ring and the nitrimino group in aromatic nitrimines is a general tendency. The deviations observed in (V) must have resulted from some non-valence inter- or intramolecular interactions, and the actual conformation is the result of a compromise between conjugation and steric hindrance. The multi-centre π-electron system, distributed over the whole molecule, renders these *N*-nitro compounds much less susceptible to nitramine rearrangement. Typical secondary aromatic nitramines can be rearranged under relatively mild conditions but their molecular structures differ from those of the aforementioned compounds in one aspect, namely, that the nitramino group is nearly perpendicular to an aromatic ring (Ejsmont *et al.*, 1998; Zaleski *et al.*, 1999).

The molecules of (III) are linked by weak C4—H4···O8 and C5—H5···N6 hydrogen bonds, forming layers in the *ac* plane (Fig. 2). Another close intermolecular contact is observed between S1 and O8^ii [3.058 (2) Å; symmetry code: (ii) $x - 1$, y, z]. This distance is significantly shorter than the sum of the van der Waals radii of 3.25 Å (Pauling, 1960) and indicates a strong interaction between the positively charged S atom in (III*c*) and the negatively charged O atom. The layers are stacked with an interlayer separation of 3.23 Å.
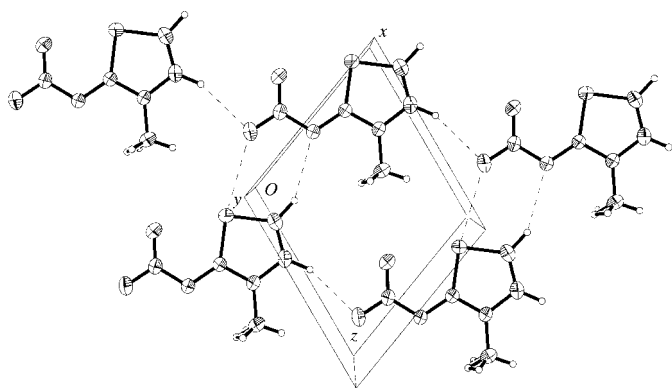

Figure 2
The packing diagram for (III), showing the hydrogen-bonding scheme viewed down the *b* axis. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

To prepare *N*-(2-thiazolyl)nitramine, (I), 2-aminothiazole (5.00 g, 0.05 mol) was dissolved in cold (*ca* 278 K) 77% sulfuric acid (15 ml). A solution of nitric acid (10.0 ml of absolute HNO$_3$, 0.25 mol) in 77% sulfuric acid (10 ml) containing sulphamic acid (1.0 g) was added dropwise with cooling. The mixture was stirred for 0.5 h at 278 K and poured onto ice (80 g). The precipitate was collected by filtration, dissolved in an alkaline (Na$_2$CO$_3$) aqueous solution, stirred with charcoal and filtered. The solution was neutralized with dilute hydrochloric acid and the precipitate was collected by filtration and crystallized from methanol (150 ml). *N*-(2-Thiazolyl)nitramine (2.92 g, 40%) was obtained as light-yellow crystals melting at 443 K with violent decomposition. Spectroscopic data for (I): MS, *m/z* (intensity): 145 (M^+, 21), 99 (100), 72 (1), 58 (9), 57 (6), 55 (40), 45 (25), 30 (4); IR (KBr, cm^{-1}): 2626–3150 (broad band with several submaxima, hydrogen-bonded N-H), 1283, 1250 (N-NO$_2$ group, nitrimine tautomeric form); ^{1}H NMR (DMSO-d_6, p.p.m.): 7.70 (*d*, 1H), 7.30 (*d*, ^3J = 4.7 Hz, 1H, aromatic protons); ^{13}C NMR (DMSO-d_6, p.p.m.): 170.3 (C2); 126.3 (C4); 112.8 (C5). To prepare 2,3-dihydro-3-methyl-2-nitriminothiazole, (III), compound (I) (5.81 g, 0.04 mol) and anhydrous potassium carbonate (5.60 g, 0.04 mol) were dissolved in water (50 ml). Dimethyl sulfate (4.7 ml, 0.05 mol) was added and the mixture was stirred at room temperature for 2 h. The precipitate was collected by filtration, washed with water and methanol, and crystallized from *N*,*N*-dimethylformamide (100 ml). Compound (III) (4.65 g, 73%), was obtained as light-orange crystals (m.p. 542–543 K) suitable for X-ray diffraction studies. Spectroscopic data for (III): MS, *m/z* (intensity): 159 (M^+, 53), 143 (1), 129 (3), 113 (100), 99 (4), 86 (29), 69 (6), 59 (3), 55 (64), 45 (23), 42 (41), 30 (10); IR (KBr, cm^{-1}): 3131, 3096, 3069, 2950 (aromatic and aliphatic protons), 1409, 1261 (N-NO$_2$ group, nitrimine group); ^{1}H NMR (DMSO-d_6, p.p.m.): 7.75 (*d*, 1H), 7.35 (*d*, ^3J = 4.7 Hz, 1H, aromatic protons), 3.72 (*s*, 3H, *N*-methyl group); ^{13}C NMR (DMSO-d_6, p.p.m.): 167.3 (C2), 131.2 (C4), 111.9 (C5), 36.8 (*N*-methyl group).

Crystal data

C$_4$H$_5$N$_3$O$_2$S	D_x = 1.679 Mg m^{-3}
M_r = 159.17	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 27
a = 6.947 (2) Å	reflections
b = 6.469 (3) Å	θ = 9–14°
c = 7.478 (3) Å	μ = 0.45 mm^{-1}
β = 110.51 (3)°	T = 295 (2) K
V = 314.8 (2) Å^3	Translucent, light orange
Z = 2	0.7 × 0.5 × 0.5 mm

Data collection

Kuma KM-4 diffractometer	$h = -9 \rightarrow 9$
ω scans	$k = -9 \rightarrow 0$
1958 measured reflections	$l = -9 \rightarrow 10$
994 independent reflections	2 standard reflections
940 reflections with $I > 2\sigma(I)$	every 50 reflections
R_{int} = 0.031	intensity decay: 0.3%
θ_{max} = 30.13°	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0563P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.034	$+ 0.0468P]$
$wR(F^2)$ = 0.097	where $P = (F_o{}^2 + 2F_c{}^2)/3$
S = 1.111	$(\Delta/\sigma)_{max} < 0.001$
994 reflections	$\Delta\rho_{max}$ = 0.44 e Å^{-3}
74 parameters	$\Delta\rho_{min}$ = −0.26 e Å^{-3}
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.716 (2)	N3—C31	1.460 (2)
S1—C5	1.718 (2)	C4—C5	1.333 (2)
C2—N3	1.340 (2)	N6—N7	1.333 (2)
C2—N6	1.349 (2)	N7—O9	1.242 (2)
N3—C4	1.382 (2)	N7—O8	1.247 (2)
C2—S1—C5	90.7 (1)	C5—C4—N3	113.2 (1)
N3—C2—N6	117.3 (1)	C4—C5—S1	111.5 (1)
N3—C2—S1	111.0 (1)	N7—N6—C2	115.0 (1)
N6—C2—S1	131.6 (1)	O9—N7—O8	121.5 (1)
C2—N3—C4	113.6 (1)	O9—N7—N6	122.8 (1)
C2—N3—C31	123.1 (1)	O8—N7—N6	115.7 (1)
C4—N3—C31	123.3 (1)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C4—H4⋯O8[i]	0.91 (3)	2.41 (3)	3.286 (3)	162 (2)
C5—H5⋯N6[ii]	0.94 (2)	2.55 (2)	3.411 (2)	154 (2)

Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $x - 1, y, z$.

The range of the refined C—H distances is 0.88 (3)–0.94 (3) Å.

Cell refinement: *Kuma Diffraction Software* (Kuma, 1997); data reduction: *Kuma Diffraction Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1113). Services for accessing these data are described at the back of the journal.

References

Bujak, M., Ejsmont, K., Kyzioł, J. B., Daszkiewicz, Z. & Zaleski, J. (1998). *Acta Cryst.* C**54**, 1945–1948.

Caranoni, P. C. & Reboul, J. P. (1982). *Acta Cryst.* B**38**, 1255–1260.

Cohen-Fernandes, P. & Habraken, C. L. (1971). *J. Org. Chem.* **36**, 3084–3086.

Daszkiewicz, Z., Kyzioł, J. B. & Zaleski, J. (1999). *J. Mol. Struct.* **513**, 69–77.

Dickey, J. B., Towne, E. B. & Wright, G. F. (1955). *J. Org. Chem.* **20**, 499–510.

Ejsmont, K., Kyzioł, J. B., Daszkiewicz, Z. & Bujaki, M. (1998). *Acta Cryst.* C**54**, 672–674.

Form, G. R., Raper, E. S. & Downie, T. C. (1974). *Acta Cryst.* B**30**, 342–348.

Kasman, S. & Taurins, A. (1956). *Can. J. Chem.* **34**, 1261–1270.

Kuma Diffraction (1997). *Kuma Diffraction Software*. Version *KM*4*b*8. Kuma Diffraction, Wrocław, Poland.

Nemes, A. & Tòth, G. (1975). *Acta Chim. Acad. Sci. Hung.* **87**, 257–267.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell University Press.

Sheldrick, G. M. (1990). *SHELXTL*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Tòth, G., Nemes, A., Tamás, J. & Volford, J. (1976). *Acta Chim. Acad. Sci. Hung.* **88**, 319–324.

Tòth, G. & Podányi, B. (1984). *J. Chem. Soc. Perkin Trans.* 2, pp. 91–94.

Zaleski, J., Daszkiewicz, Z. & Kyzioł, J. B. (1998). *Acta Cryst.* C**54**, 1687–1689.

Zaleski, J., Daszkiewicz, Z. & Kyzioł, J. B. (1999). *Acta Cryst.* C**55**, 1292–1295.