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4-Methyl-2-[*N*-(3,4-methylenedioxybenzylidene)hydrazino]thiazole and its reduction product, 4-methyl-2-[*N*-(3,4-methylenedioxybenzylidene)hydrazono]-4,5-dihydrothiazole

Johan Wouters,[a]* Bernadette Norberg[a] and Salvatore Guccione[b]

[a]Laboratoire Chimie Moléculaire Structurale, Facultés Universitaires Notre-Dame de la Paix, 61 Rue de Bruxelles, B-5000 Namur, Belgium, and [b]Dipartimento di Scienze Farmaceutiche, Università Catania, Viale A. Doria 6, Ed. 2 (ex Ed. 12) Cittá Universitaria, I-95125 Catania, Italy
Correspondence e-mail: johan.wouters@fundp.ac.be

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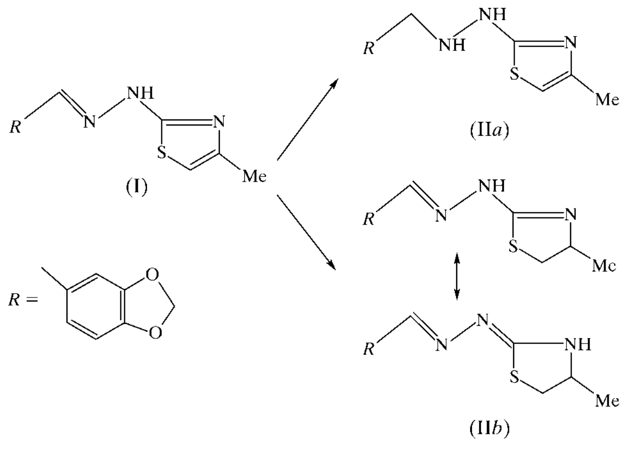
The crystal structures of 4-methyl-2-[*N*-(3,4-methylenedioxybenzylidene)hydrazino]thiazole, $C_{12}H_{11}N_3O_2S$, and its reduction product 4-methyl-2-[*N*-(3,4-methylenedioxybenzylidene)hydrazono]-4,5-dihydrothiazole, $C_{12}H_{13}N_3O_2S$, have been determined and compared. In the reduction product, the tautomer observed bears an H atom on the exocyclic N atom. Both compounds form hydrogen-bonded dimers over centers of inversion.

Comment

The reduction of 4-methyl-2-[*N*-(3,4-methylenedioxybenzylidene)hydrazino]thiazole, (I), has been reported to lead to the corresponding benzyl analogue (II) (Mazzone *et al.*, 1992; Pignatello *et al.*, 1994; Cambria *et al.*, 1996; Gritsch *et al.*, 2001). Determination of the crystal structures of both compounds has been undertaken in order to clarify the mechanism of reduction of (I). The structural evidence given in this work demonstrates that the product of the reaction is the (II*b*) isomer. The crystal structure further establishes that the tautomeric form of this product is the one with an H atom on the endocyclic N3 atom.



Both compounds adopt an extended conformation (Fig. 1), with torsion angles N3—C4—N6—N7 [−177.53 (14) and 176.72 (19)° for (I) and (II*b*), respectively], C4—N6—N7—C8 [179.46 (15) and 171.73 (18)°] and N6—N7—C8—C9 [179.9 (2) and 177.6 (2)°] close to 180°. A similar *anti-E* conformation is observed for related substituted thiazol-2-ylhydrazines in solution, as demonstrated by NMR data and *ab initio* calculations in water (Wouters *et al.*, 2002).

For the fully oxidized molecule, (I), analysis of the bond lengths and angles confirm an sp^2 hybridation of all C and N atoms of the benzylidenehydrazinothiazole fragment. The C1—C2 [1.345 (3) Å], C2—N3 [1.394 (2) Å], N3—C4 [1.3071 (19) Å], C4—N6 [1.356 (2) Å], N6—N7 [1.3714 (18) Å] and N7—C8 [1.276(2) Å] bond lengths are intermediate between C—C or C—N single and double bonds. The alternation of shorter and longer bonds further confirms electron delocalization along the whole molecule.

In the reduced product (II), atoms C1 and C2 adopt a tetrahedral (sp^3) geometry, as demonstrated by the C2—C1—S5 [107.37 (15)°] and C1—C2—N3 [104.93 (18)°] valence

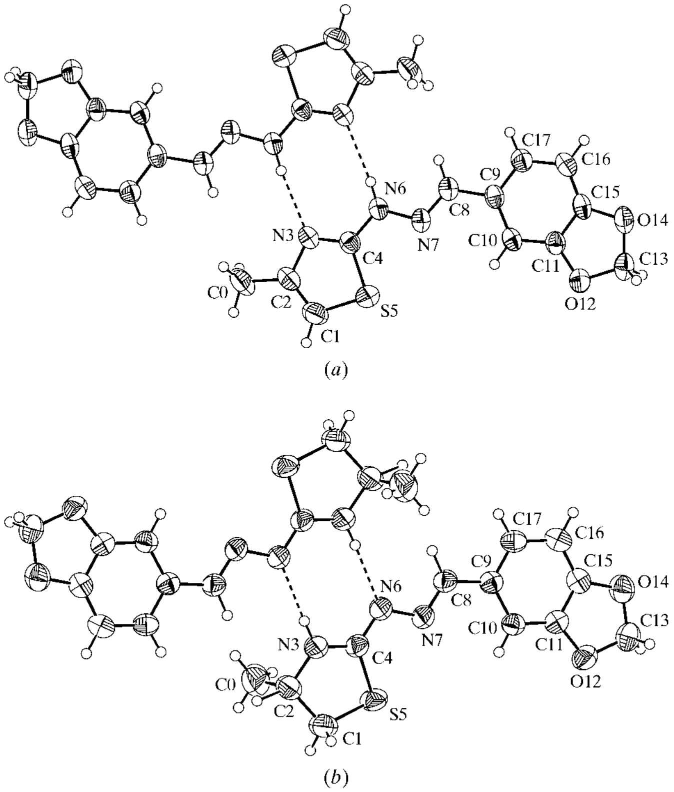


Figure 1
Views of the dimers formed in the crystal structures of (*a*) compound (I) and (*b*) compound (II*b*). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and the atom-numbering scheme is given.

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angles. The C1—C2 bond [1.533 (3) Å] is significantly longer that the corresponding bond in (I). In (II), the C4—N3 bond [1.339 (3) Å] is also longer than the C4—N6 bond [1.294 (3) Å]. The opposite is observed in (I). Analysis of the geometry therefore strongly suggests that the structure of the reduction product of (I) is the (II*b*) isomer and not (II*a*).

Unambiguous localization from the difference Fourier map of an H atom on the endocyclic N3 atom in (II) establishes the tautomeric preference of the reduction product. Recent results obtained by energy calculations at the HF/6-31G(d) and MP2/6-31G(d) levels confirm the stability of the endocyclic N3 tautomeric form (Wouters *et al.*, 2002).

In compound (II), the H atom on the endocyclic N3 atom is involved in a hydrogen bond connecting N3 to N6 [N3···N6 3.005 (2) Å; see Table 4]. As a consequence of this hydrogen bond, molecules form interesting dimers in the crystal packing, as illustrated in Fig. 1.

A similar dimeric assembly is observed in the crystal structure of compound (I). The same N atoms are involved in the stabilization *via* a hydrogen bond. In contrast to structure (II), the H-atom donor in (I) is the exocyclic N6 atom [N6···N3 3.048 (2) Å; see Table 2].

Experimental

Details of the synthesis of the title compounds are given in Mazzone *et al.* (1992), Pignatello *et al.* (1994) and Cambria *et al.* (1996).

Compound (I)

Crystal data

$C_{12}H_{11}N_3O_2S$
$M_r = 261.31$
Monoclinic, $P2_1/n$
$a = 6.219\ (1)$ Å
$b = 12.163\ (2)$ Å
$c = 15.855\ (1)$ Å
$\beta = 91.13\ (1)^\circ$
$V = 1199.1\ (3)$ Å^3
$Z = 4$
$D_x = 1.447$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 35$–45°
$\mu = 2.40$ mm^{-1}
$T = 293\ (2)$ K
Plate, yellow
$0.60 \times 0.40 \times 0.09$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical (North *et al.*, 1968)
$T_{\min} = 0.393$, $T_{\max} = 0.805$
3882 measured reflections
2356 independent reflections
2066 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 71.9^\circ$
$h = 0 \rightarrow 7$
$k = -11 \rightarrow 14$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Table 1
Selected geometric parameters (Å, °) for (1).

N3—C4	1.3071 (19)	N7—C8	1.276 (2)
N3—C2	1.394 (2)	C1—C2	1.345 (3)
N6—N7	1.3714 (18)	C8—C9	1.457 (2)
N6—C4	1.356 (2)		
C2—N3—C4	109.33 (14)	N3—C2—C1	115.26 (16)
N7—N6—C4	116.11 (13)	N3—C4—N6	124.03 (14)
N6—N7—C8	116.83 (14)	N7—C8—C9	122.30 (15)
S5—C1—C2	111.24 (14)		

Table 2
Hydrogen-bonding geometry (Å, °) for (1).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···N3$^{\rm i}$	0.86	2.19	3.048 (2)	172

Symmetry code: (i) $2 - x, -y, 1 - z$.

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.106$
$S = 1.09$
2356 reflections
164 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.2929P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Compound (II*b*)

Crystal data

$C_{12}H_{13}N_3O_2S$
$M_r = 263.32$
Monoclinic, $P2_1/c$
$a = 14.738\ (1)$ Å
$b = 5.750\ (1)$ Å
$c = 15.898\ (1)$ Å
$\beta = 105.02\ (1)^\circ$
$V = 1301.2\ (3)$ Å^3
$Z = 4$
$D_x = 1.344$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 35$–45°
$\mu = 2.21$ mm^{-1}
$T = 293\ (2)$ K
Prism, yellow
$0.60 \times 0.40 \times 0.21$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical (North *et al.*, 1968)
$T_{\min} = 0.336$, $T_{\max} = 0.660$
3758 measured reflections
2540 independent reflections
2333 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 71.9^\circ$
$h = -18 \rightarrow 17$
$k = -7 \rightarrow 5$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Table 3
Selected geometric parameters (Å, °) for (2*b*).

C1—C2	1.533 (3)	N6—N7	1.394 (2)
C2—N3	1.441 (3)	N7—C8	1.267 (3)
N3—C4	1.339 (3)	C8—C9	1.459 (3)
C4—N6	1.294 (3)		
C2—C1—S5	107.37 (16)	C8—N7—N6	114.15 (16)
C4—N3—C2	117.19 (17)	N7—C8—C9	122.54 (17)
N6—C4—N3	122.62 (17)		

Table 4
Hydrogen-bonding geometry (Å, °) for (2*b*).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···N6$^{\rm i}$	0.87	2.14	3.005 (2)	175

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 0.3517P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R(F) = 0.042$	$(\Delta/\sigma)_{\max} = 0.001$
$wR(F^2) = 0.135$	$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$S = 1.11$	$\Delta\rho_{\min} = -0.25$ e Å^{-3}
2540 reflections	Extinction correction: *SHELXL* (Sheldrick, 1997)
167 parameters	Extinction coefficient: 0.0035 (5)
H-atom parameters not refined	

The H atoms on N3 or N6 were located at the end of the refinement in a Fourier difference synthesis. Once located, they were refined as riding (N—H = 0.87 and 0.86 Å, respectively). All other H atoms were refined as riding, with C—H distances in the range 0.93–0.97 Å.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1506). Services for accessing these data are described at the back of the journal.

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