Table 3. *Torsion angles (°) in ring E of the title compound compared with corresponding angles in related compounds*

C22 configuration	(I) S^a	(II) S^b	(III) R^c	(IV) R^d	(III) S^c	(IV) S^d	(V) S^e	(VI)^f
C22—O16—C16—C17	14.6	13.9	18.7	12.0	−24.8	−33.2	−30.8	15.2
C22—O17—C17—C16	−28.9	−29.1	−27.3	−28.3	−5.5	−2.8	−15.6	−18.8
O16—C16—C17—O17	8.9	9.6	5.4	10.4	18.2	21.9	26.9	2.2
C16—O16—C22—O17	−33.7	−33.3	−36.8	−30.3	21.9	32.7	23.3	−26.9
C17—O17—C22—O16	39.5	39.5	40.3	36.9	−9.2	−17.8	−3.6	28.0
Mean e.s.d.'s	0.3	0.5	0.4	0.5	0.5	0.8	3.6	0.6

References: (*a*) present work; (*b*) Pniewska, Anulewicz & Uszycka-Horawa (1995); (*c*) Pniewska, Anulewicz, Uszycka-Horawa & Kroszczyński (1995); (*d*) Albertsson, Oskarsson & Svensson (1978); (*e*) Krakower, Keeler & Gougoutas (1971); (*f*) Surcouf (1979), C22 is not chiral.

The absolute configuration was assigned to agree with the known configuration of the main steroid skeleton. The hydroxyl H11O atom was found in a difference map and refined isotropically. All other H atoms were refined with riding models.

Data collection: *Kuma KM*-4 *Software* (Kuma, 1991). Cell refinement: *Kuma KM*-4 *Software*. Data reduction: *Kuma KM*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-*tert*-Butylthiazolidine-2-thione and 5-Phenylthiazolidine-2-thione

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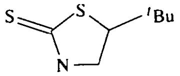
Abstract

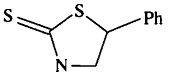
In the title compounds, $C_7H_{13}NS_2$, (I), and $C_9H_9NS_2$, (II), the heterocycle adopts a half-chair conformation with a torsion angle τ = S1—C5—C4—N3 equal to 27.5 (4)° in (I) and 30.0 (3)° in (II). In both crystals, a hydrogen bond between the thione group and the N atom is observed, the corresponding S2···N3 distance being equal to 3.367 (8) Å in (I) and 3.376 (9) Å in (II).

Comment

This report completes a series of papers devoted to a conformational study of the substituted thiazolidine-2-thione family, hereafter TH-2 TH (Laknifli, Pierrot, Chanon & Chanon, 1995, and references therein). The present paper is concerned with two derivatives in position 5: 5-*tert*-butyl-TH-2 TH, compound (I) and 5-phenyl-TH-2 TH, compound (II).



(I)



(II)

An *ORTEP*II (Johnson, 1976) view of the molecules and the atom-numbering schemes is shown in Fig. 1. Bond distances and angles are comparable with

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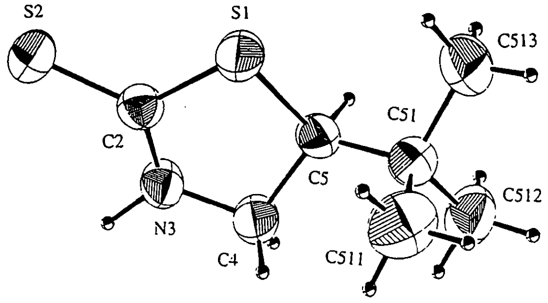
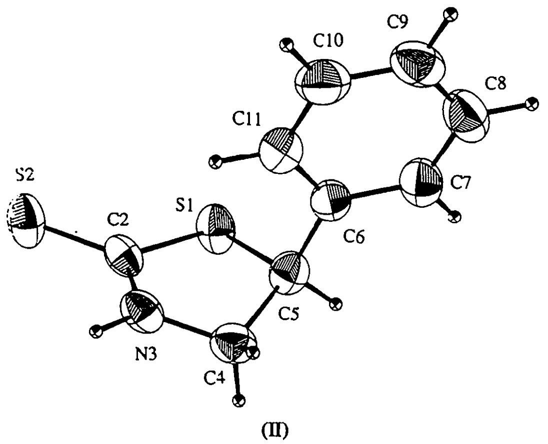
values found in this series of compounds (Laknifli, Pierrot, Chanon & Chanon, 1995). In both structures, the conformation of the heterocycle is unchanged: the S1—C2—S2—N3 fragment is planar with C4 on one side and C5 on the other side of the fragment (Table 4). Therefore, the heterocycle adopts a half-chair conformation and the torsion angle τ = S1—C5—C4—N3 is equal to 27.5 (4)° for (I) and 30.0 (3) for (II).

The packing of the molecules in crystals (I) and (II) is indicated in Fig. 2. In both crystals, a short intermolecular contact between S2 of one molecule and N3 of a neighbouring molecule is observed (Table 3). Owing to the lower electronegativity of the S than the O atom, an N—H···S bond is weaker than an N—H···O bond and hydrogen bonding between a thione group and an N atom is not common, but this observation has already been made in the TH-2 TH series (Laknifli, Pierrot, Chanon & Chanon, 1995), and in a series of dithione structures (Mizuguchi & Rihs, 1992; Mizuguchi, Arita & Rihs, 1991; Mizuguchi, Rochat & Rihs, 1990). A strong intermolecular bond is generally linear, to within 10°. The bond-forming power decreases as the atoms deviate from linearity (0.42 kJ mol^{-1} per 6°; Pauling, 1960). The values of N3—H3···S2 in compounds (I) and (II) are favourable for the formation of hydrogen bonds.

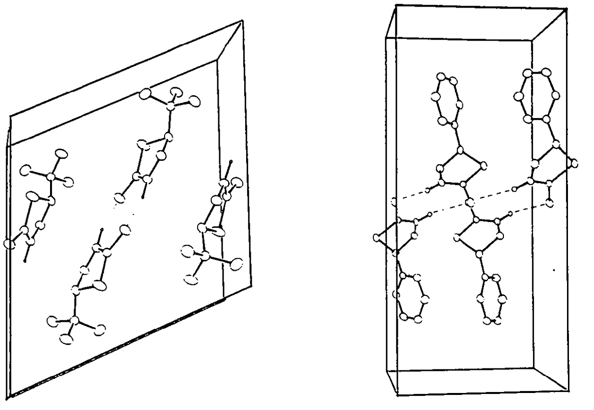


(I)



(II)

Fig. 1. *ORTEP*II (Johnson, 1976) view of the title compounds with ellipsoids at 50% probability and the atomic numbering scheme.



(I) (II)

Fig. 2. Molecular packing in crystals (I) and (II). The hydrogen bonds between N3 and S2 are indicated. For clarity, only four molecules have been included in the unit cell of (2).

Experimental

These compounds were prepared according to the procedure described by Bafford, Chanon & Metzger (1973). Crystals were obtained by evaporation at room temperature of 50:50 benzene–cyclohexane solution.

Compound (I)

Crystal data

$C_7H_{13}NS_2$
M_r = 175.32
Monoclinic
$P2_1/c$
a = 12.848 (4) Å
b = 6.356 (3) Å
c = 12.391 (4) Å
β = 113.48 (5)°
V = 928 (1) $Å^3$
Z = 4
D_x = 1.255 Mg m^{-3}

D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 14–16°
μ = 0.485 mm^{-1}
T = 293 K
Rectangular prism
0.6 × 0.4 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1877 measured reflections
1408 independent reflections
1068 observed reflections [$I > 3\sigma(I)$]

R_{int} = 0.027
θ_{max} = 25°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 7$
$l = -14 \rightarrow 14$
3 standard reflections frequency: 3600 min intensity decay: 1.3%

Refinement

Refinement on F
R = 0.050
wR = 0.0486
S = 0.91
1068 reflections
91 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.528 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.536 e $Å^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (II)

Crystal data

$C_9H_9NS_2$
$M_r = 195.31$
Orthorhombic
Pbca
$a = 10.480$ (3) Å
$b = 8.926$ (3) Å
$c = 19.503$ (6) Å
$V = 1824$ (2) Å^3
$Z = 8$
$D_x = 1.422$ Mg m^{-3}

D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14$–16°
$\mu = 0.502$ mm^{-1}
$T = 293$ K
Rectangular prism
0.6 × 0.5 × 0.3 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1876 measured reflections
1636 independent reflections
1118 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.032$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 22$
3 standard reflections frequency: 3600 min intensity decay: 1.8%

Refinement

Refinement on F
$R = 0.038$
$wR = 0.040$
$S = 1.223$
1118 reflections
109 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\rm max} = 0.03$
$\Delta\rho_{\rm max} = 0.546$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.612$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I) and (II)*

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Compound (I)				
S1	0.8876 (1)	0.0725 (1)	0.59895 (5)	3.70 (2)
S1	0.2574 (1)	0.1576 (2)	0.1137 (1)	5.75 (3)
S2	0.4161 (1)	0.2956 (2)	0.0082 (1)	4.90 (3)
C4	0.3570 (3)	−0.2151 (7)	0.1599 (4)	4.1 (1)
C51	0.1801 (3)	−0.1793 (7)	0.2091 (3)	3.84 (9)
C511	0.2179 (4)	−0.3585 (8)	0.2977 (4)	5.8 (1)
N3	0.4152 (3)	−0.0745 (6)	0.1099 (3)	3.79 (8)
C2	0.3719 (3)	0.1145 (7)	0.0768 (3)	3.52 (9)
C5	0.2873 (3)	−0.0788 (7)	0.2068 (3)	3.66 (9)
C512	0.1187 (4)	−0.0151 (9)	0.2523 (4)	6.1 (1)
C513	0.0998 (4)	−0.262 (1)	0.0907 (5)	6.4 (2)
Compound (II)				
S2	0.6969 (1)	−0.0363 (1)	0.49656 (6)	4.09 (2)
C2	0.8217 (3)	−0.0666 (4)	0.5470 (2)	2.91 (7)
N3	0.8877 (3)	−0.1924 (3)	0.5525 (1)	3.26 (6)
C7	0.9961 (4)	−0.0639 (4)	0.7733 (2)	3.82 (8)
C5	0.9884 (4)	−0.0607 (4)	0.6452 (2)	3.27 (7)
C4	1.0034 (4)	−0.1891 (4)	0.5940 (2)	3.67 (8)
C11	0.8253 (4)	−0.1928 (5)	0.7189 (2)	4.02 (8)
C9	0.8432 (4)	−0.1988 (5)	0.8412 (2)	4.42 (9)
C6	0.9341 (3)	−0.1049 (4)	0.7138 (2)	3.07 (7)
C10	0.7809 (4)	−0.2391 (5)	0.7823 (2)	4.54 (9)
C8	0.9508 (4)	−0.1100 (5)	0.8369 (2)	4.53 (9)

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

	(I)	(II)
S1—C2	1.727 (5)	1.745 (3)
S1—C5	1.839 (4)	1.829 (4)
S2—C2	1.660 (5)	1.659 (4)
N3—C2	1.319 (5)	1.323 (4)
N3—C4	1.452 (6)	1.458 (5)
C4—C5	1.518 (7)	1.529 (5)
C2—S1—C5	92.8 (2)	93.0 (2)
S1—C2—S2	121.8 (2)	122.7 (2)
S2—C2—N3	127.1 (4)	126.8 (3)
C2—N3—C4	117.9 (4)	117.6 (3)
N3—C4—C5	107.1 (4)	107.0 (3)
C4—C5—S1	103.5 (3)	103.0 (2)

Table 3. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
Compound (I)				
N3—H3···S2$^{\rm i}$	1.06 (1)	2.336 (6)	3.367 (8)	164.1 (2)
Compound (II)				
N3—H3···S2$^{\rm ii}$	0.98 (1)	2.432 (6)	3.376 (9)	168.3 (2)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, z$.

Table 4. *Distance (Å) to the S1—C2—S2—N3 fragment and value of the torsion angle τ (°)*

	(I)	(II)
C4	+0.115 (4)	+0.145 (4)
C5	−0.355 (4)	−0.367 (4)
τ	+27.5 (4)	+30.0 (3)

Program used for data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Program used throughout the analysis: CAD-4 *SDP-Plus* (Frenz, 1985). Program used to solve the structures: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, (1982) completed by Fourier synthesis. H atoms located on difference Fourier or calculated at idealized positions were introduced in the calculations before the last refinement cycle but not refined. Refinement was by full-matrix least-squares methods including anisotropic displacement parameters for all non-H atoms. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1284). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 218–219

Structures of Chiral Nitrones. II. (*Z*)-*N*-[(2*S*)-2-(*tert*-Butoxycarbonylamino)propylidene]benzylamine *N*-Oxide

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(*Received 26 May 1995; accepted 10 July 1995*)

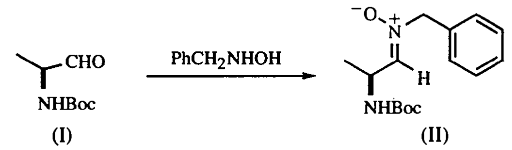
Abstract

The structure of the title compound, $C_{15}H_{22}N_2O_3$, was determined and the C—CH=N$^+$(O$^-$)C nitrone system shown to be planar. The configuration of the nitrone is confirmed to be *Z*. The molecular packing involves an intermolecular hydrogen bond of 2.915 (3) Å between the N atom of the carbonylamino group and the O atom of the *N*-oxide group.

Comment

During the course of a research program aimed at the synthesis of efficient nitrogen-containing electrophiles of synthetic utility, we have described general procedures for the preparation of both aldehyde- (Dondoni, Franco, Junquera, Merchan, Merino & Tejero, 1994) and ketone-derived nitrones (Franco, Merchan, Merino & Tejero, 1995). The title compound (II) was prepared from the α-aminoaldehyde (I) following these procedures. Its crystal structure was determined in order to confirm the configuration of the unsaturated nitrone system.

The absolute configuration of (II) was not considered since the starting aldehyde (I) was enantiomerically pure having an *S* configuration at the only asymmetric center. The molecular geometry and numbering scheme of (II) are shown in Fig. 1. The most interesting feature from a geometrical point of view is the planarity of the C—CH=N$^+$(O$^-$)C nitrone system which is confirmed to have a *Z* configuration; the O1—N1—C1—C2 and O1—N1—C1—H1 torsion angles are 5.0 (4) and −175°, respectively. The carbamate moiety is also planar [N2—C11—O2—O3 −177.8 (2)°]. No appreciable differences are observed between the bond lengths and angles of the nitrone function and those of other non-chiral (Bedford, Chaloner & Hitchcock, 1991) and chiral (Merino, Merchan, Tejero & Lanaspa, 1995) nitrones.



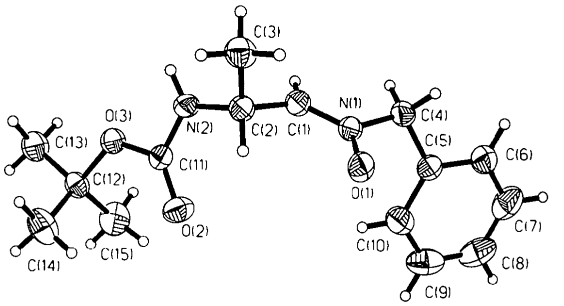


Fig. 1. Molecular geometry and the numbering scheme for the title compound. Displacement ellipsoids are plotted at the 30% probability level.

No intramolecular hydrogen bonds are observed but intermolecular hydrogen-bond interactions are present. An intermolecular hydrogen bond [N2—H···O1($-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) 2.915 (3) Å] is observed. The packing in the crystal (shown in Fig. 2) is also influenced by van der Waals forces between the aromatic rings which are separated by 2.602 (4) Å.

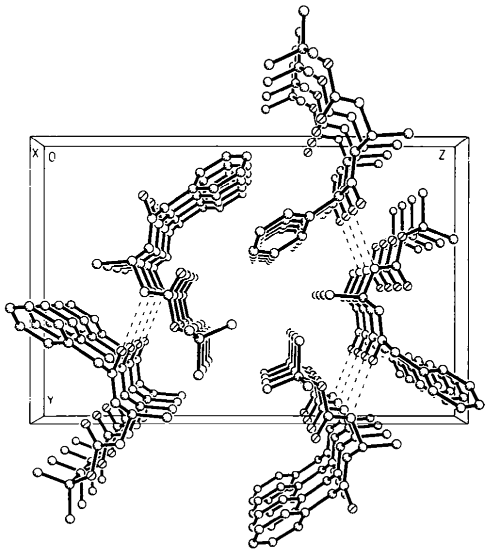


Fig. 2. Crystal packing of (II) along the shortest axis *a*, with the *c* axis horizontal.