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Acta Cryst. (1994). **C50**, 1828–1830

A Novel Bis-Tetrahydronaphthyl Thiosemicarbazone

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(Received 5 January 1994; accepted 27 May 1994)

Abstract

In an attempt to produce 2-methylene-1-tetralone thiosemicarbazone, the reaction of 2-methylene-1-tetralone with thiosemicarbazide in ethanol containing catalytic quantities of acetic acid afforded the title compound, 2-[2-(2-hydroxy-1-oxo-1,2,3,4-tetrahydro-2-naphthyl)ethyl]-1,2,3,4-tetrahydronaphthalen-1-one 1-thiosemicarbazone, C₂₃H₂₅N₃O₂S, whose structure is reported here. The configuration of the carbimino group

is *E* and the bond lengths in the thiosemicarbazone groups indicate delocalization of the electrons of the N atoms. The planes of the aryl groups are approximately parallel to each other. One of the two cyclohexenone rings is in a twist-chair conformation and the other is in a twist-boat conformation.

Comment

Recently, the anticonvulsant activity of a number of Mannich bases has been described (Dimmock, Jonnalagadda, Phillips, Erciyas, Shyam & Semple, 1992). These compounds are known to undergo facile demethylation, producing the corresponding α,β -unsaturated ketones (Tramontini & Angiolini, 1990) which may be the moieties responsible for bioactivity. Since various thiosemicarbazones have displayed anticonvulsant properties (Dimmock, McColl, Wonko, Thayer & Hancock, 1991), the synthesis of thiosemicarbazones of conjugated enones such as (2) was considered with the aim of producing novel, prototypic anticonvulsant agents. However, reaction of (1) with thiosemicarbazide produced (3) as indicated in the scheme below. The structure of (3) is reported here and Fig. 1 shows an *ORTEPII* (Johnson, 1976) diagram of this compound.

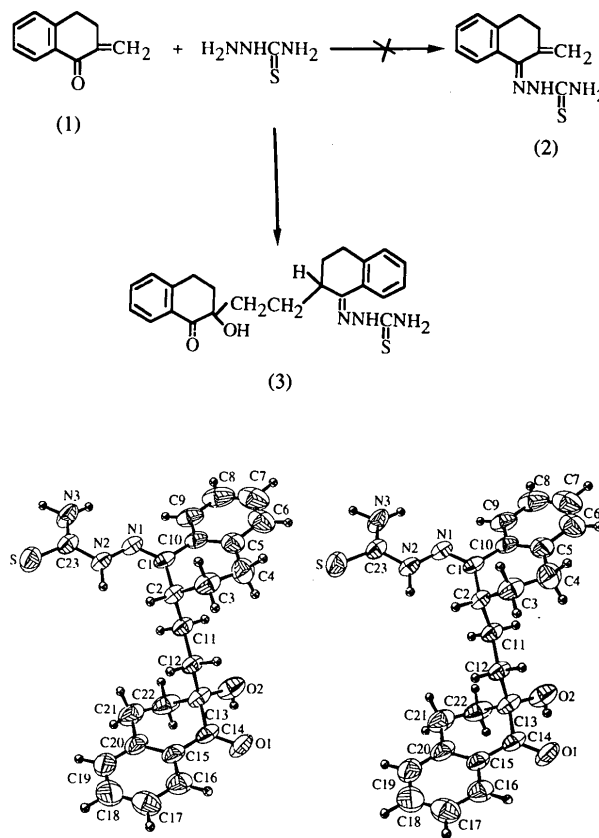


Fig. 1. A stereoscopic *ORTEPII* (Johnson, 1976) view of the title compound. Displacement ellipsoids are plotted at the 50% probability level.

The carbimino group has an *E* configuration. The C1=N1 and N1—N2 bond lengths are 1.285 (3) and 1.376 (3) Å, respectively. These values are at the upper and lower limits, respectively, of the lengths of the C=N double bond and the N—N single bond present in various thiosemicarbazones and thiosemicarbazides (Gabe, Taylor, Glusker, Menken & Patterson, 1969; Restivo & Palenik, 1970; Mathew & Palenik, 1971*a,b*; Andreotti, Domiano, Gasparri, Nardelli & Sgarabotto, 1970; Kálmán, Argay & Czugler, 1972; Czugler, Kálmán & Argay, 1973; Palenik, Rendle & Carter, 1974; Dimmock *et al.*, 1990). These data suggest that the π electrons of the C1=N1 double bond are partially delocalized over the N1—N2 single bond. Under this condition, the C1=N1 bond is slightly longer than a pure C=N double bond. The C23—N2 and C23—N3 bond lengths of 1.354 (3) and 1.320 (3) Å are very close to the weighted averages of the two corresponding C—N bonds of 1.350 (4) and 1.318 (4) Å, respectively, in the various thiosemicarbazones (Palenik, Rendle & Carter, 1974). The reason that these two C—N bonds are shorter than a pure C—N single bond is the delocalization of the lone pairs of electrons on N2 and N3 over the C23—N2 and C23—N3 bonds, respectively. The difference between these two bonds is reasonable, since in the case of N3 a primary amino group (NH₂) is present, while for N2 a secondary amine (NH) is attached to another N atom. The C23—S bond length is 1.669 (3) Å which is at the short end of C=S double-bond distances [1.670 (4)–1.706 (6) Å] found in other thiosemicarbazones (Gabe, Taylor, Glusker, Menken & Patterson, 1969; Restivo & Palenik, 1970; Mathew & Palenik, 1971*a,b*; Palenik, Rendle & Carter, 1974; Dimmock *et al.*, 1990).

Both aryl rings are planar and their planes are approximately parallel. The distance between the centers of the two rings is 4.925 (14) Å. The (C1,C2,C3,C4,C5,C10) cyclohexenone ring is in a twist-chair configuration whereas the conformation of the (C13,C14,C15,C20,C21,C22) cyclohexenone ring is a twist boat. The side chain C1—N1—N2—C23—S—N3 is not planar. The C1—N1—N2 and N2—C23—S—N3 planes make a dihedral angle of 9.87 (9)°. The two chiral atoms C2 and C13 are in *R* and *S* conformations, respectively, in the enantiomer selected for the asymmetric unit (asymmetric units *x,y,z*). The molecules form into clusters through intermolecular O1...HN3A—N3 hydrogen bonds.

Experimental

Crystal data

C₂₃H₂₅N₃O₂S
M_r = 407.53
 Monoclinic
*P*2₁/*a*

Mo *K*α radiation
 $\lambda = 0.7107$ Å
 Cell parameters from 25 reflections

a = 10.492 (4) Å
b = 13.048 (3) Å
c = 15.595 (2) Å
 $\beta = 99.54$ (3)°
V = 2105.2 (11) Å³
Z = 4
D_x = 1.286 Mg m⁻³
D_m = 1.287 Mg m⁻³
D_m measured by flotation in bromoform/butanol

$\theta = 7.00$ – 19.50°
 $\mu = 0.17$ mm⁻¹
T = 289 K
 Prism
 0.73 × 0.25 × 0.13 mm
 Light pink

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 4212 measured reflections
 3702 independent reflections
 2671 observed reflections
 $[I_{\text{net}} > 1.0\sigma(I_{\text{net}})]$

*R*_{int} = 0.011
 $\theta_{\text{max}} = 24.93^\circ$
h = $-12 \rightarrow 12$
k = $0 \rightarrow 15$
l = $0 \rightarrow 18$
 3 standard reflections
 frequency: 120 min
 intensity variation: none

Refinement

Refinement on *F*
R = 0.049
wR = 0.050
S = 2.47
 2671 reflections
 262 parameters
 H-atom parameters not refined
 $w = 1/[\sigma^2(F) + 0.00008F^2]$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S	0.68174 (8)	0.33120 (6)	0.18805 (6)	0.0812 (5)
O1	0.49635 (19)	1.05963 (12)	0.22812 (14)	0.0776 (13)
O2	0.31184 (18)	0.92564 (13)	0.24066 (14)	0.0817 (14)
N1	0.44190 (18)	0.46001 (13)	0.31941 (13)	0.0506 (12)
N2	0.53219 (20)	0.44679 (13)	0.26566 (13)	0.0549 (12)
N3	0.47678 (21)	0.27807 (15)	0.25633 (16)	0.0722 (16)
C1	0.43259 (21)	0.54882 (16)	0.35344 (15)	0.0460 (13)
C2	0.50910 (21)	0.64341 (16)	0.34007 (15)	0.0463 (13)
C3	0.56525 (25)	0.68571 (19)	0.42932 (17)	0.0624 (15)
C4	0.4616 (3)	0.71364 (22)	0.48066 (17)	0.0769 (19)
C5	0.3603 (3)	0.63216 (22)	0.47997 (17)	0.0628 (16)
C6	0.2832 (3)	0.6326 (3)	0.54366 (19)	0.0832 (21)
C7	0.1873 (4)	0.5620 (4)	0.54282 (25)	0.100 (3)
C8	0.1637 (3)	0.4898 (3)	0.4771 (3)	0.0940 (25)
C9	0.2405 (3)	0.48698 (21)	0.41329 (20)	0.0715 (18)
C10	0.34212 (22)	0.55685 (18)	0.41560 (17)	0.0529 (14)
C11	0.42363 (23)	0.71836 (16)	0.28104 (15)	0.0504 (13)
C12	0.49563 (23)	0.81525 (16)	0.26348 (15)	0.0519 (14)
C13	0.4162 (3)	0.89097 (17)	0.20093 (17)	0.0578 (15)
C14	0.5048 (3)	0.97997 (18)	0.18899 (17)	0.0572 (15)
C15	0.6003 (3)	0.96463 (18)	0.13057 (16)	0.0579 (15)
C16	0.7045 (3)	1.03202 (20)	0.13529 (18)	0.0669 (17)
C17	0.7960 (3)	1.0178 (3)	0.08299 (21)	0.0806 (21)
C18	0.7825 (4)	0.9388 (3)	0.02472 (22)	0.0913 (24)
C19	0.6797 (4)	0.87350 (24)	0.01779 (19)	0.0878 (24)
C20	0.5868 (3)	0.88345 (19)	0.07161 (18)	0.0705 (18)
C21	0.4756 (4)	0.80915 (21)	0.06671 (18)	0.0871 (22)
C22	0.3674 (3)	0.84660 (21)	0.11149 (19)	0.0780 (18)
C23	0.55598 (25)	0.35098 (17)	0.23899 (16)	0.0560 (14)

Table 2. Selected geometric parameters (Å, °)

S—C23	1.669 (3)	C7—C8	1.384 (7)
O1—C14	1.216 (3)	C8—C9	1.380 (5)
O2—C13	1.418 (3)	C9—C10	1.399 (4)
N1—N2	1.376 (3)	C11—C12	1.521 (3)
N1—C1	1.285 (3)	C12—C13	1.534 (3)
N2—C23	1.354 (3)	C13—C14	1.519 (3)
N3—C23	1.320 (3)	C13—C22	1.519 (4)
C1—C2	1.505 (3)	C14—C15	1.475 (4)
C1—C10	1.469 (3)	C15—C16	1.396 (4)
C2—C3	1.522 (3)	C15—C20	1.394 (4)
C2—C11	1.528 (3)	C16—C17	1.371 (5)
C3—C4	1.498 (4)	C17—C18	1.366 (6)
C4—C5	1.502 (4)	C18—C19	1.364 (6)
C5—C6	1.381 (4)	C19—C20	1.394 (5)
C5—C10	1.395 (4)	C20—C21	1.509 (5)
C6—C7	1.363 (6)	C21—C22	1.509 (5)
N2—N1—C1	118.15 (18)	O2—C13—C14	110.03 (19)
N1—N2—C23	118.92 (19)	O2—C13—C22	110.83 (22)
N1—C1—C2	127.11 (21)	C12—C13—C14	106.93 (20)
N1—C1—C10	116.02 (20)	C12—C13—C22	113.80 (20)
C2—C1—C10	116.79 (20)	C14—C13—C22	107.40 (22)
C1—C2—C3	107.76 (19)	O1—C14—C13	119.66 (25)
C1—C2—C11	109.57 (18)	O1—C14—C15	122.67 (23)
C3—C2—C11	114.74 (18)	C13—C14—C15	117.66 (22)
C2—C3—C4	111.82 (21)	C14—C15—C16	119.22 (23)
C3—C4—C5	113.53 (23)	C14—C15—C20	120.4 (3)
C4—C5—C6	119.3 (3)	C16—C15—C20	120.4 (3)
C4—C5—C10	121.07 (23)	C15—C16—C17	120.2 (3)
C6—C5—C10	119.6 (3)	C16—C17—C18	119.5 (3)
C5—C6—C7	120.7 (3)	C17—C18—C19	121.1 (3)
C6—C7—C8	120.5 (3)	C18—C19—C20	121.1 (3)
C7—C8—C9	119.9 (3)	C15—C20—C19	117.6 (3)
C8—C9—C10	119.8 (3)	C15—C20—C21	121.0 (3)
C1—C10—C5	119.92 (22)	C19—C20—C21	121.4 (3)
C1—C10—C9	120.65 (24)	C20—C21—C22	113.78 (23)
C5—C10—C9	119.38 (25)	C13—C22—C21	112.54 (24)
C2—C11—C12	112.40 (19)	S—C23—N2	119.31 (18)
C11—C12—C13	114.60 (19)	S—C23—N3	124.06 (19)
O2—C13—C12	107.76 (21)	N2—C23—N3	116.63 (23)

H atoms were placed in calculated positions on the corresponding O atom (O—H = 0.85 Å), C atoms (C—H = 1.00 Å) and N atoms (N—H = 1.00 Å), and were not refined. The U_{iso} of each H atom was assigned to be $U_{eq} + 0.01$ of the corresponding O, N or C atom.

The ω -scan width was $(1.10 + 0.35 \tan \theta)^\circ$ with a θ -scan rate of $0.69\text{--}5.49^\circ \text{ min}^{-1}$. The scan angle was extended 25% on each side of each peak for background measurement. Refinement was by full-matrix least-squares methods.

Data collection and cell refinement: Enraf-Nonius CAD-4 software. Data reduction: DATRD2 NRCVAX (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: SOLVER NRCVAX. Program(s) used to refine structure: LSTSQ NRCVAX. Molecular graphics: ORTEP NRCVAX (Johnson, 1976). Software used to prepare material for publication: TABLES NRCVAX; UTILITY NRCVAX.

We thank the Natural Sciences and Engineering Council of Canada for providing funds (to JWQ) for an X-ray diffractometer and operating grant. We also thank Nordic Merrell Dow Research Inc., Laval, Quebec, Canada, for financial support of this work and the University of Saskatchewan for the award of a graduate scholarship (to JY). SNP thanks Banaras Hindu University for the award of a sabbatical leave and the Canadian Bureau of International Education for a fellowship enabling him to work at the University of Saskatchewan.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the IUCr (Reference: CR1128). 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. (1994). C50, 1830–1832

N,N'-Carbonylbis(L-phenylalanine ethyl ester)

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(Received 31 August 1993; accepted 4 January 1994)

Abstract

The title compound, C₂₃H₂₈N₂O₅, is a symmetrical urea derivative with a twofold rotation axis coincident with the carbonyl group [C(1)=O(1)]. Its structure is characterized by a long planar region (14 Å) from which two phenyl rings project out at about 45°. In addition, two O atoms are positioned between the phenyl rings and are separated by about 7 Å. The orientation of the phenyl rings may explain the moderate inhibitory effect of this derivative.