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Acta Cryst. (1994). **C50**, 635–638

Cyclohexanone Semicarbazone and 4-*tert*-Butylcyclohexanone Semicarbazone

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(Received 21 July 1992; accepted 6 September 1993)

Abstract

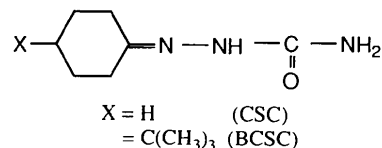
Cyclohexanone semicarbazone (CSC), $C_7H_{13}N_3O$, and 4-*tert*-butyl-cyclohexanone (BCSC), $C_{11}H_{21}N_3O$, each adopt a slightly distorted chair conformation, with an increase of the total puckering of the six-membered ring for BCSC. The two crystal structures are very similar, with the $NHCONH_2$ groups connected in infinite ribbons through $O\cdots H-N$ hydrogen bonds, with distances in the range 2.84–3.12 Å. The conformation adopted by the $C=O$ bond with respect to the $N-N$ bond is *trans* in both crystals.

Comment

It is usually found in the crystal structures of uncomplexed thiosemicarbazones that the $C=S$ bond is

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trans to the $N-N$ bond, and this *trans* conformation is retained in semicarbazones, the only exception being acetone semicarbazone (Naik & Palenik, 1974). Since it has not been established what factors determine the *cis/trans* conformation of the semicarbazide fragment in semicarbazones, the title compounds were chosen for an X-ray investigation to provide more structural information on this class of compounds.



The ring conformation of each compound can be described as a slightly distorted chair flattened at the $C=N$ apex (Figs. 1 and 2), allowing the $C(2)-C(1)-C(6)$ bond angle to increase to $115.7(2)^\circ$ for

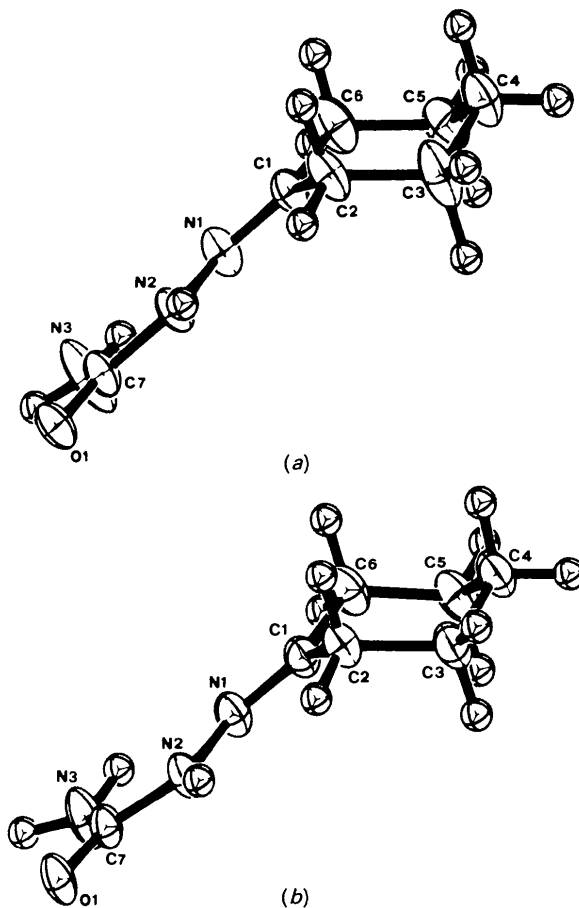


Fig. 1. Drawings of (a) molecule A and (b) molecule B in the crystal of cyclohexanone semicarbazone (CSC) showing the anisotropy of the thermal motion. The displacement ellipsoids of the non-H atoms have been scaled to the 30% probability level. The drawing is based on the atomic parameters from the final refinement.

CSC and to 113.6(4)° for BCSC, while the other internal angles remain close to the corresponding values found in cyclohexane [$111.4 \pm 0.2^\circ$ (Bastiansen, Fernholt, Seip, Kambara & Kuchitsu, 1973)]. In BCSC, the values of 108.2(5)° for C(3)—C(4)—C(5), 114.6(5)° for C(3)—C(4)—C(8) and 114.5(5)° for C(5)—C(4)—C(8) show that the steric strain caused by the presence of a bulky substituent is minimized by slight deformations in the skeleton of the six-membered ring. A similar angular deformation of the cyclohexane ring has been observed in many other 4-*tert*-butylcyclohexane derivatives (van Koningsveld, 1972; James & Grainger, 1972; Chiaroni, Riche & Pascard-Billy, 1974; Lectard, Lichanot, Metras, Gaultier & Hauw, 1975; Doesburg, Petit & Merckx, 1982; Reetz, Schweltnus, Hübner, Massa & Schmidt, 1983; van Koningsveld & Jansen, 1984; Labar, Krier, Norberg, Evrard & Durant, 1985; Mariezcurrena & Fornaro, 1988). The C—C bond lengths do not show appreciable differences from the mean values obtained from the Cambridge Structural Database (CSD; Allen *et al.*, 1987) for C_{sp³}—C_{sp²} [1.507(15) Å] and C_{sp³}—C_{sp³} [1.535(16) Å] bonds in cyclohexane derivatives.

The staggered conformation assumed by the equatorial *tert*-butyl group of BCSC is in agreement with MM2 force-field calculations (Burkert & Allinger, 1982) and with those found from the CSD for similar compounds (van Koningsveld & Jansen, 1984).

In both compounds, the semicarbazone group has a conformation in which the C=O bond is *trans* to the N—N bond. From Figs. 3 and 4 it may be seen that, although both compounds have three atoms capable of hydrogen bonding, only two of them are

utilized. The participation of all three H atoms in hydrogen bonding has been observed only in acetone semicarbazone (Naik & Palenik, 1974), and it has been suggested that the uncommon *cis* conformation of the semicarbazone group found in this molecule could be dependent on the hydrogen-bonding pattern. In CSC and BCSC, the terminal NHCONH₂ group forms dimer units involving the hydrazine and

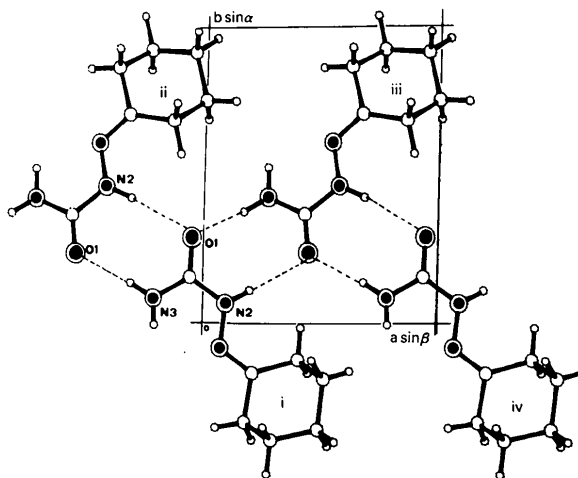


Fig. 3. Projection of the crystal structure down *c* in cyclohexanone semicarbazone (CSC). The symmetry operations relating the two independent molecules in the asymmetric unit [(i) molecule *A* at *x*, *y*, *z* and (ii) molecule *B* at *x*, *y*, *z*] to the other molecules are: (iii) molecule *B*, 1 + *x*, *y*, *z*; (iv) molecule *A*, 1 + *x*, *y*, *z*. O and N atoms of the semicarbazone moieties are represented by filled circles. The hydrogen bonds are indicated by dashed lines.

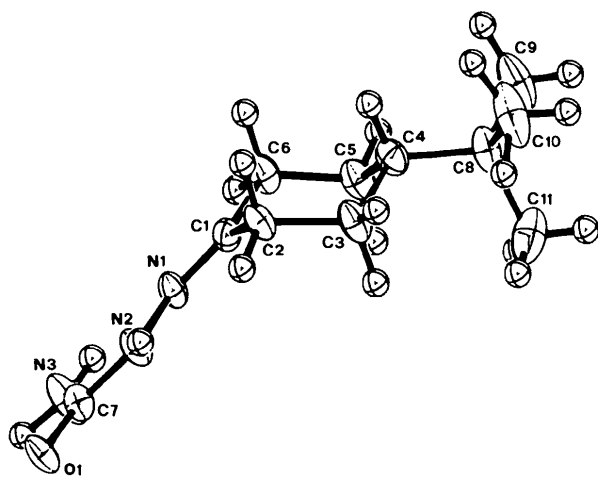


Fig. 2. A drawing of the 4-*tert*-butylcyclohexanone semicarbazone molecule (BCSC) showing the anisotropy of the thermal motion. The displacement ellipsoids of the non-H atoms have been scaled to the 30% probability level. The drawing is based on the atomic parameters from the final refinement.

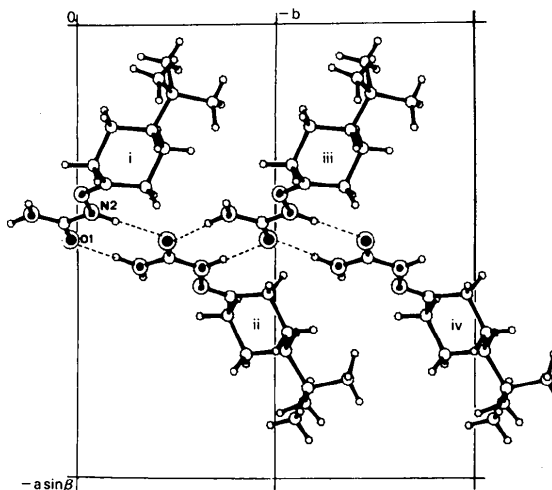


Fig. 4. Projection of the crystal structure down *c* in 4-*tert*-butylcyclohexanone semicarbazone (BCSC). The symmetry operations relating the various molecules are: (i) *x*, *y*, *z*; (ii) 1 - *x*, 0.5 + *y*, 0.5 - *z*; (iii) *x*, -1 + *y*, *z*; (iv) 1 - *x*, -0.5 + *y*, 0.5 - *z*. O and N atoms of the semicarbazone moieties are represented by filled circles. The hydrogen bonds are indicated by dashed lines.

the amide groups *via* intermolecular O...H—N hydrogen bonds, with O...N distances in the range 2.84–3.12 (2) Å in CSC and 2.88–3.10 (5) Å in BCSC. This gives rise to undulated ribbons of molecules which run parallel to the shortest axes of the cells, with adjacent ribbons being held together by van der Waals forces. A preliminary communication of the present work has been given (Portalone *et al.*, 1988).

Experimental

CSC

Crystal data

C₇H₁₃N₃O

M_r = 155.20

Triclinic

P $\bar{1}$

a = 7.346 (1) Å

b = 10.632 (1) Å

c = 11.986 (1) Å

α = 64.85 (1)°

β = 88.31 (1)°

γ = 89.31 (1)°

V = 847.0 (2) Å³

Z = 4

D_x = 1.217 Mg m⁻³

D_m = 1.223 Mg m⁻³

Cu *K*α radiation

λ = 1.5418 Å

Cell parameters from 24 reflections

θ = 31–50°

μ = 0.70 mm⁻¹

T = 293 K

Tablets

0.38 × 0.38 × 0.08 mm

Colourless

Data collection

Syntex P2₁ diffractometer

$\omega/2\theta$ scans

Absorption correction:

none

4733 measured reflections

2995 independent reflections

2265 observed reflections

$[|F_o| > 3\sigma|F_o|]$

R_{int} = 0.035

θ_{\max} = 69°

h = 0 → 8

k = -12 → 12

l = -14 → 14

3 standard reflections

monitored every 100

reflections

intensity variation: <4.5%

Refinement

Refinement on *F*

R = 0.0399

wR = 0.0450

S = 0.1

2265 reflections

303 parameters

All H-atom parameters

refined

$w = 1/(26.0 + F_o + 0.028F_o^2)$

$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.1 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.1 \text{ e } \text{Å}^{-3}$

Data collection

Syntex P2₁ diffractometer

$\omega/2\theta$ scans

Absorption correction:

none

3847 measured reflections

2587 independent reflections

1089 observed reflections

$[|F_o| > 3\sigma|F_o|]$

R_{int} = 0.0563

θ_{\max} = 30°

h = 0 → 18

k = 0 → 10

l = -14 → 14

3 standard reflections

monitored every 100

reflections

intensity variation: <4.0%

Refinement

Refinement on *F*

R = 0.060

wR = 0.0671

S = 0.2

1089 reflections

199 parameters

Only coordinates of H atoms refined

$w = 1/(100.0 + |F_o| + 0.001|F_o|^2)$

$(\Delta/\sigma)_{\max} = 0.02$

$\Delta\rho_{\max} = 0.1 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.2 \text{ e } \text{Å}^{-3}$

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

CSC	$B_{\text{eq}} = (4/3)\sum_i\sum_j\beta_{ij}a_i \cdot a_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{eq}</i>
Molecule A				
O(1)	-0.0990 (2)	0.2631 (1)	0.4923 (1)	4.17 (4)
N(1)	0.0115 (2)	-0.0780 (2)	0.6907 (2)	4.20 (5)
N(2)	0.0380 (2)	0.0604 (2)	0.6123 (1)	3.67 (5)
N(3)	-0.2711 (2)	0.0769 (2)	0.6055 (2)	7.67 (9)
C(1)	0.1490 (2)	-0.1560 (2)	0.7365 (2)	3.63 (6)
C(2)	0.3450 (3)	-0.1155 (2)	0.7169 (2)	4.71 (7)
C(3)	0.4433 (4)	-0.1745 (3)	0.8384 (3)	6.81 (10)
C(4)	0.4158 (3)	-0.3296 (2)	0.9093 (3)	5.56 (8)
C(5)	0.2157 (4)	-0.3618 (3)	0.9343 (2)	5.62 (8)
C(6)	0.1110 (3)	-0.3067 (2)	0.8150 (3)	5.52 (8)
C(7)	-0.1130 (2)	0.1400 (2)	0.5655 (2)	3.67 (5)
Molecule B				
O(1)	-0.6016 (2)	0.2156 (1)	0.5061 (1)	4.60 (5)
N(1)	-0.4844 (2)	0.5519 (2)	0.2961 (2)	4.08 (5)
N(2)	-0.4615 (2)	0.4189 (2)	0.3873 (2)	3.88 (5)
N(3)	-0.7620 (2)	0.3844 (2)	0.3602 (2)	5.62 (7)
C(1)	-0.3547 (3)	0.6398 (2)	0.2689 (2)	3.81 (6)
C(2)	-0.1697 (3)	0.6201 (2)	0.3222 (2)	4.21 (7)
C(3)	-0.0206 (3)	0.6801 (2)	0.2225 (2)	4.86 (8)
C(4)	-0.0617 (3)	0.8277 (2)	0.1296 (2)	5.19 (8)
C(5)	-0.2447 (4)	0.8355 (3)	0.0730 (2)	5.65 (8)
C(6)	-0.3950 (3)	0.7834 (2)	0.1714 (3)	5.54 (8)
C(7)	-0.6105 (2)	0.3342 (2)	0.4221 (2)	3.63 (6)
BCSC				
O(1)	-0.5006 (2)	0.0908 (4)	-0.2749 (3)	4.1 (1)
N(1)	-0.3760 (2)	-0.0238 (5)	0.0115 (4)	3.5 (1)
N(2)	-0.4256 (3)	-0.0510 (5)	-0.1064 (4)	3.6 (1)
N(3)	-0.4305 (3)	0.2577 (6)	-0.1166 (5)	5.7 (2)
C(1)	-0.3469 (3)	-0.1597 (6)	0.0779 (4)	3.4 (1)
C(2)	-0.3564 (3)	-0.3564 (6)	0.0474 (5)	3.6 (1)
C(3)	-0.2706 (4)	-0.4509 (8)	0.0648 (5)	4.5 (2)
C(4)	-0.2185 (3)	-0.4163 (7)	0.1960 (5)	4.0 (1)
C(5)	-0.2089 (4)	-0.2130 (7)	0.2142 (5)	4.3 (2)
C(6)	-0.2950 (4)	-0.1221 (8)	0.2049 (5)	4.3 (2)
C(7)	-0.4548 (3)	0.1009 (7)	-0.1704 (5)	3.6 (1)
C(8)	-0.1355 (3)	-0.5224 (7)	0.2207 (6)	4.8 (2)
C(9)	-0.0906 (5)	-0.4817 (12)	0.3565 (9)	7.9 (3)
C(10)	-0.1554 (5)	-0.7257 (11)	0.2176 (10)	8.5 (3)
C(11)	-0.0762 (5)	-0.4774 (14)	0.1239 (10)	8.4 (3)

BCSC

Crystal data

C₁₁H₂₁N₃O

M_r = 211.31

Monoclinic

P2₁/c

a = 16.029 (5) Å

b = 7.431 (2) Å

c = 10.518 (2) Å

β = 97.91 (2)°

V = 1240.9 (6) Å³

Z = 4

D_x = 1.131 Mg m⁻³

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 8–12°

μ = 0.08 mm⁻¹

T = 293 K

Tablets

0.40 × 0.40 × 0.10 mm

Colourless

Table 2. Bond distances (Å) and angles (°)

	CSC		
	Molecule A	Molecule B	BCSC
O(1)—C(7)	1.231 (3)	1.237 (6)	1.237 (6)
N(3)—C(7)	1.320 (3)	1.331 (3)	1.330 (7)
N(2)—C(7)	1.367 (3)	1.363 (3)	1.363 (6)
N(2)—N(1)	1.382 (3)	1.382 (3)	1.393 (5)
N(1)—C(1)	1.278 (3)	1.277 (3)	1.278 (6)
C(1)—C(2)	1.491 (3)	1.493 (3)	1.500 (7)
C(2)—C(3)	1.520 (5)	1.526 (4)	1.533 (7)
C(3)—C(4)	1.513 (5)	1.521 (5)	1.534 (7)
C(4)—C(5)	1.506 (4)	1.509 (4)	1.527 (8)
C(5)—C(6)	1.524 (5)	1.516 (4)	1.528 (8)
C(6)—C(1)	1.499 (4)	1.509 (4)	1.500 (7)
C(4)—C(8)			1.538 (7)
C(8)—C(9)			1.539 (10)
C(8)—C(10)			1.543 (10)
C(8)—C(11)			1.522 (12)
O(1)—C(7)—N(3)	123.1 (2)	122.4 (2)	122.3 (5)
O(1)—C(7)—N(2)	121.1 (2)	120.6 (2)	120.6 (4)
N(3)—C(7)—N(2)	115.8 (2)	116.9 (2)	117.0 (5)
N(1)—N(2)—C(7)	117.7 (2)	117.1 (2)	115.7 (4)
N(2)—N(1)—C(1)	119.7 (2)	119.6 (2)	119.5 (4)
N(1)—C(1)—C(2)	127.5 (2)	128.6 (2)	129.4 (4)
N(1)—C(1)—C(6)	116.8 (2)	115.6 (2)	117.1 (4)
C(2)—C(1)—C(6)	115.7 (2)	115.7 (2)	113.6 (4)
C(1)—C(2)—C(3)	110.9 (3)	111.9 (2)	111.0 (4)
C(2)—C(3)—C(4)	112.4 (2)	112.7 (2)	113.5 (5)
C(3)—C(4)—C(5)	109.8 (2)	111.0 (2)	108.2 (5)
C(4)—C(5)—C(6)	111.3 (3)	111.1 (3)	110.7 (5)
C(5)—C(6)—C(1)	112.1 (2)	111.7 (2)	111.1 (4)
C(3)—C(4)—C(8)			114.6 (5)
C(5)—C(4)—C(8)			114.5 (5)
C(4)—C(8)—C(9)			109.8 (5)
C(4)—C(8)—C(10)			109.1 (5)
C(4)—C(8)—C(11)			112.3 (6)
C(9)—C(8)—C(10)			106.3 (6)
C(9)—C(8)—C(11)			108.8 (6)
C(10)—C(8)—C(11)			110.3 (6)

For both compounds data were corrected for Lorentz and polarization effects but not for absorption. The structures were determined by direct methods with *SIR88* (Burla *et al.*, 1989) and refined by anisotropic full-matrix least squares. The H atoms were localized from final difference Fourier syntheses and refined isotropically. For BCSC the isotropic temperature factor of the H atoms was arbitrarily fixed to the corresponding value of the attached non-H atoms. There are no significant differences between the two crystallographically independent molecules of CSC. Calculations were carried out on a Data General Eclipse MV/8000 II using mainly *SIRCAOS* (Camalli *et al.*, 1986). Some of the final calculations were performed with *PARST* (Nardelli, 1983). The scattering factors used were those of Cromer & Mann (1968) for the non-H atoms and those of Hanson, Herman, Lea & Skillman (1964) for the H atoms.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates for CSC and BCSC, and complete geometry for CSC have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71616 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR1006]

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Acta Cryst. (1994). **C50**, 638–640

1,1';2,2'-Bis- μ -dimethylsilyl-bis[1,2-dicarba-closo-dodecaborane(12)], C₈H₃₂B₂₀Si₂

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(Received 20 April 1993; accepted 15 September 1993)

Abstract

The molecule is situated across the center of inversion. Two *closo*-carbaborane cages are joined by two Si bridges with Si—C bonds of 1.907 (3) and 1.914 (3) Å.