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1-(Cycloheptyl)thiosemicarbazide crystal structure

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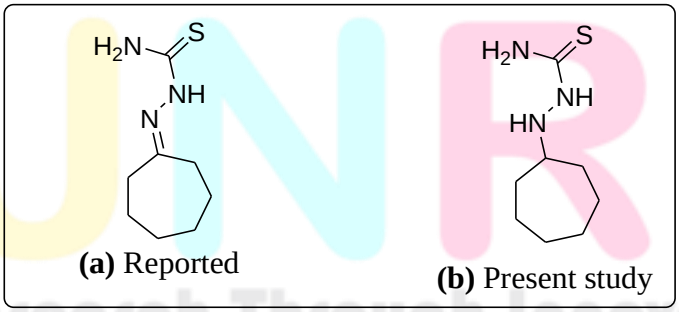
Abstract: In the present work we have synthesized the 1-(Cycloheptyl)thiosemicarbazide by the greener and eco-friendly protocols. The chromatographically pure compound was allowed to single crystal growth using the ethylacetate and hexane (1:1) mixture. The crystal structure study was done for the titled compound $C_8H_{17}N_3S$ molecular weight 187.32 Da, the crystal system has interlocked dimers formed through weak intramolecular diagonal interactions of N---H---N and N---H---S, and the crystal is stabilized by C---H---π interaction.

Introduction: Triazole is a five-membered heterocyclic molecule with three nitrogen and two carbon atoms in a ring. Which is highly employed in pharmaceutical industries (Shafran *et al.* 2008). The chemistry of 1,2,4-triazoles bearing moiety play an important role with fused heterocyclic moiety are often found wide range of therapeutically interesting such as anti-HIV (Alvarez, *et al.* 1994), anti-viral (Witkowski, *et al.* 1973), anti-depressant (Demirbas, *et al* 2004), anti-cancer (Pagliai, *et al* 2006),



(a) Reported **(b)** Present study

Figure 1: (a) Structure of 1-(Cycloheptylidene) thiosemicarbazide **(b)** 1-(Cycloheptyl)thiosemicarbazide

anti-epileptic (Hakimian *et al* 2007), analgesic (Jin, *et al* 2007), anti-allergic (Buckle, *et al* 1986) and ant-tubercular (Yaseen *et al* 2004). Moreover, these analogous have been employed very much in agrochemicals due to their plant growth regulatory action. In literature only limited number of synthetic methods are available for the synthesis of 1,2,4-triazolidine-3-thiones (Victor *et al* 2005). In the present work we aiming to prepare 2-Cycloheptyl -1,2,4-triazolidine-3-thiones, but crystal study obtained shows open structure of 1-(Cycloheptyl)thiosemicarbazide. The molecule is synthesized by novel green chemistry protocol employing agro-

waste extract as a catalytic solvent media by the reaction of cycloheptane with thiosemicarbazide under room temperature stirring conditions. After a simple reaction workup the product was extracted and crystallized.

1. Structural commentary

The **Table 1** represents crystallographic data and X-ray structure parameters. Measurements were made using Bruker SMART CCD area-detector diffractometer with monochromatic Mo *K*α radiation at room temperature. The crystalline state of a crystal is characterized by a long range, well-defined three-dimensional orders.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT[R]; program(s) used to solve structure: SHELXS97; molecular graphics: ORTEP-3; software used to prepare material for publication: SHELXL97. E-map provided positions for all non-H-atoms. The full-matrix least-squares refinement was carried out on F^2 using anisotropic temperature factors for all non-H-atoms. The H-atoms were located from DF-maps, and then their positions were refined using a riding model with isotropic thermal parameters taken as 1.2 times temperature factors for their parent atoms. The ORTEPs of these isomers were obtained by the PLATON program. Crystals of 1-(Cycloheptyl)thiosemicarbazide were obtained using chloroform and ethanol mixture (9:1) by slow evaporation at room temperature and the crystalline state is characterized by a long-range, well-defined three-dimensional orders. The asymmetric unit contains two independent molecules as depicted in **Figure 2.** The 2-cycloheptylhydrazine ring system is nearly planar. The dihedral angle between two 2-cycloheptylhydrazine rings is 8.22 (12)°. In the crystal, weak intramolecular N---H.....N and intermolecular N---H.....S hydrogen bonds are observed C---H…π interactions help to stabilize the crystal packing. Bond lengths and angles are within the normal ranges.

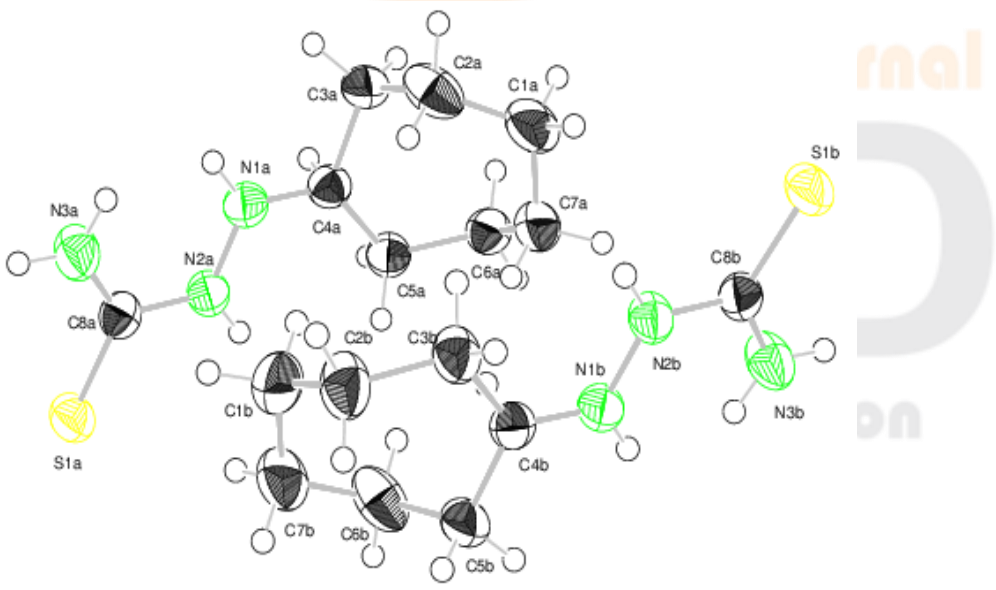


Figure 2: The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

2. Synthesis and crystallization

The synthesis of 1-cycloheptylhydrazine carbothioamide is carried out *via* the reaction of heptanone (2 mmol) and thiosemicarbazide (2 mmol) in presence of agro-waste derived catalytic media WEOFSA (Water Extract of Orange Fruit peel Ash) under magnetic stirring condition for about 1 h (Khatavi *et al* un published data). The completion of the reaction was monitored by TLC, after completion of the reaction, product extracted using the ethyl acetate and concentrated under reduced pressure. The powder obtained is dissolved in chloroform and ethanol mixture (9:1) and it is allowed to slow evaporation for about one week at room temperature, the fine glassy crystals of 1-(Cycloheptyl)thiosemicarbazide is separated and structure was predicted by the single X-ray crystallography.

3. Refinement

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4540 / 0 / 218
Goodness-of-fit on F^2	1.056
Final R indices [I>2σ(I)]	R1 = 0.0619, wR2 = 0.1765
R indices (all data)	R1 = 0.0756, wR2 = 0.1936
Weighting scheme	$\omega = 1/[\sigma^2(F_o^2) + (0.0714P)^2 + 0.2386P]$ *Where* $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) max	< 0.001
Largest diff. peak and hole	0.420 and -0.760 e.Å^{-3}

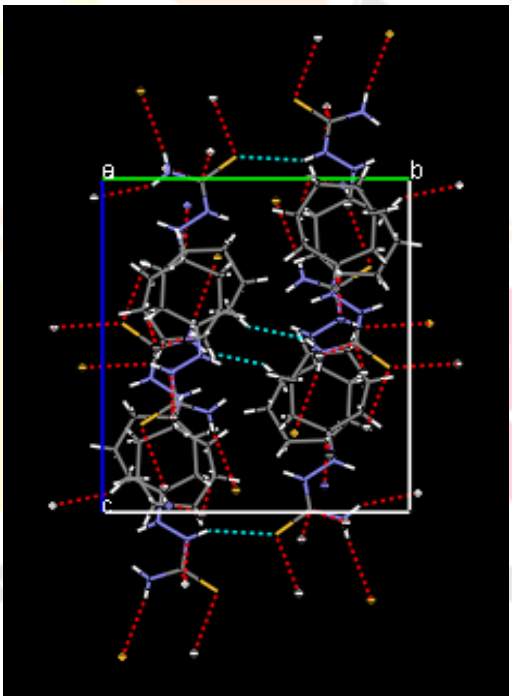


Figure 3. A view of the packing in the title molecule, Dashed lines indicate N---H---S intermolecular interactions diagonally along [001] 3D network structure.

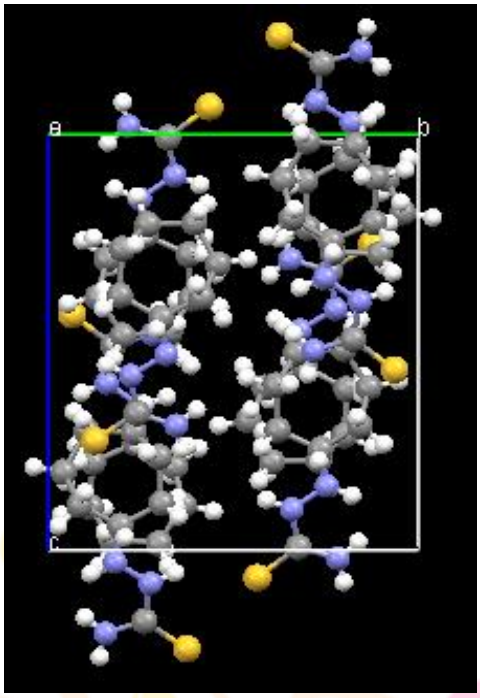


Figure 4: A view of the packing in the title molecule in unit cell stick model

Acknowledgement

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Supporting information

Table 1: Crystal data, Data collection and Structure refinement

Empirical formula	$C_8 H_{17} N_3 S$
Formula weight	187.32
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 12.738(10 Å b = 11.714(8) Å c = 13.359(10) Å α = 90.00 °, β= 92.253(9) ° γ = 90.00 °
Volume	1992(3) Å ^{3}
Z	4
Calculated density	1.042 mg/m^3
Crystal size	0.22 × 0.15 × 0.12 mm
Absorption coefficient	0.072 mm^{-1}
F(000)	664
Crystal form	Prism, colorless
Radiation source	fine-focus sealed tube
Radiation type	Mo *Kα*
Radiation monochromator	graphite
Criterion for observed reflection	I > 2σ(I)
Data collection	
Diffractometer	Bruker SMART CCD area-detector
Data collection method	ω- χ scans
Absorption correction	multi-scan
Theta range for data collection	3.05 to 27.51 °
Limiting indices	-16<=h<=11, -15<=k<=14, -13<=l<=17
Reflections collected / unique	11320 / 4540 [R(int) = 0.0633]
Completeness to theta	99.2 %
Max. and min. transmission	T_{max} = 1.000, T_{min} = 0.790

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 2-Cycloheptylhydrazine carbothioamide. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1B)	3623(1)	4353(1)	-663(1)	54(1)
S(1A)	3289(1)	1252(1)	7373(1)	51(1)
N(1B)	4774(2)	2474(2)	1549(1)	41(1)
N(2A)	2384(2)	2241(2)	5800(1)	43(1)
N(2B)	4455(2)	3418(2)	985(1)	42(1)
N(3B)	3826(2)	2170(2)	-198(2)	56(1)
N(1A)	1998(2)	3192(2)	5290(1)	45(1)
C(6A)	1239(2)	1999(2)	2755(2)	49(1)
C(8A)	2873(2)	2396(2)	6706(2)	40(1)
N(3A)	3012(2)	3458(2)	7000(2)	55(1)
C(4A)	1586(2)	3062(2)	4409(2)	40(1)
C(3A)	1187(2)	4148(2)	3915(2)	51(1)
C(4B)	5173(2)	2641(2)	2428(2)	39(1)
C(8B)	3984(2)	3240(2)	73(2)	40(1)
C(5A)	1506(2)	1939(2)	3875(2)	43(1)
C(2B)	5764(3)	3848(2)	3966(2)	61(1)
C(5B)	5498(2)	1581(2)	2996(2)	53(1)
C(3B)	5321(2)	3800(2)	2890(2)	49(1)
C(1A)	1807(2)	3957(3)	2125(2)	64(1)
C(7B)	5189(3)	2014(3)	4839(2)	64(1)
C(7A)	2018(2)	2689(3)	2162(2)	60(1)
C(6B)	4863(3)	1342(3)	3911(2)	65(1)
C(1B)	5081(3)	3296(3)	4739(2)	72(1)
C(2A)	1909(2)	4587(2)	3117(2)	61(1)

Table 3. Bond lengths [A] and angles [deg] for kspr.

S(1B)-C(8B)	1.687(2)	C(1A)-H(1A2)	0.9700
S(1A)-C(8A)	1.683(2)	C(7B)-C(6B)	1.512(4)
N(1B)-C(4B)	1.277(3)	C(7B)-C(1B)	1.513(5)
N(1B)-N(2B)	1.390(3)	C(7B)-H(7B1)	0.9700
N(1B)-H(1B)	0.8600	C(7B)-H(7B2)	0.9700
N(2A)-C(8A)	1.351(3)	C(7A)-H(7A1)	0.9700
N(2A)-N(1A)	1.386(3)	C(7A)-H(7A2)	0.9700
N(2A)-H(2A)	0.8600	C(6B)-H(6B1)	0.9700
N(2B)-C(8B)	1.354(3)	C(6B)-H(6B2)	0.9700
N(2B)-H(2B)	0.8600	C(1B)-H(1B1)	0.9700
N(3B)-C(8B)	1.318(3)	C(1B)-H(1B2)	0.9700
N(3B)-H(3B1)	0.8600	C(2A)-H(2A1)	0.9700
N(3B)-H(3B2)	0.8600	C(2A)-H(2A2)	0.9700
N(1A)-C(4A)	1.278(3)	C(4B)-N(1B)-N(2B)	118.26(18)
N(1A)-H(1A)	0.8600	C(4B)-N(1B)-H(1B)	120.9
C(6A)-C(5A)	1.524(3)	N(2B)-N(1B)-H(1B)	120.9
C(6A)-C(7A)	1.525(4)	C(8A)-N(2A)-N(1A)	118.31(18)
C(6A)-H(6A1)	0.9700	C(8A)-N(2A)-H(2A)	120.8
C(6A)-H(6A2)	0.9700	N(1A)-N(2A)-H(2A)	120.8
C(8A)-N(3A)	1.314(3)	C(8B)-N(2B)-N(1B)	118.33(18)
N(3A)-H(3A1)	0.8600	C(8B)-N(2B)-H(2B)	120.8
N(3A)-H(3A2)	0.8600	N(1B)-N(2B)-H(2B)	120.8
C(4A)-C(5A)	1.498(3)	C(8B)-N(3B)-H(3B1)	120.0
C(4A)-C(3A)	1.511(3)	C(8B)-N(3B)-H(3B2)	120.0
C(4A)-H(4A)	0.9800	H(3B1)-N(3B)-H(3B2)	120.0
C(3A)-C(2A)	1.524(4)	C(4A)-N(1A)-N(2A)	118.84(19)
C(3A)-H(3A1)	0.9700	C(4A)-N(1A)-H(1A)	120.6
C(3A)-H(3A2)	0.9700	N(2A)-N(1A)-H(1A)	120.6
C(4B)-C(3B)	1.500(3)	C(5A)-C(6A)-C(7A)	114.2(2)
C(4B)-C(5B)	1.505(3)	C(5A)-C(6A)-H(6A1)	108.7
C(4B)-H(4B)	0.9800	C(7A)-C(6A)-H(6A1)	108.7
C(5A)-H(5A1)	0.9700	C(5A)-C(6A)-H(6A2)	108.7
C(5A)-H(5A2)	0.9700	C(7A)-C(6A)-H(6A2)	108.7

C(2B)-C(1B)	1.521(4)	H(6A1)-C(6A)-H(6A2)	107.6
C(2B)-C(3B)	1.525(4)	N(3A)-C(8A)-N(2A)	116.6(2)
C(2B)-H(2B1)	0.9700	N(3A)-C(8A)-S(1A)	123.99(18)
C(2B)-H(2B2)	0.9700	N(2A)-C(8A)-S(1A)	119.41(17)
C(5B)-C(6B)	1.518(4)	C(8A)-N(3A)-H(3A1)	120.0
C(5B)-H(5B1)	0.9700	C(8A)-N(3A)-H(3A2)	120.0
C(5B)-H(5B2)	0.9700	H(3A1)-N(3A)-H(3A2)	120.0
C(3B)-H(3B1)	0.9700	N(1A)-C(4A)-C(5A)	124.1(2)
C(3B)-H(3B2)	0.9700	N(1A)-C(4A)-C(3A)	114.9(2)
C(1A)-C(7A)	1.510(4)	C(5A)-C(4A)-C(3A)	121.07(19)
C(1A)-C(2A)	1.518(5)	N(1A)-C(4A)-H(4A)	90.3
C(1A)-H(1A1)	0.9700	C(5A)-C(4A)-H(4A)	90.3
C(3A)-C(4A)-H(4A)	90.3	H(1A1)-C(1A)-H(1A2)	107.4
C(4A)-C(3A)-C(2A)	112.8(2)	C(6B)-C(7B)-C(1B)	115.1(2)
C(4A)-C(3A)-H(3A1)	109.0	C(6B)-C(7B)-H(7B1)	108.5
C(2A)-C(3A)-H(3A1)	109.0	C(1B)-C(7B)-H(7B1)	108.5
C(4A)-C(3A)-H(3A2)	109.0	C(6B)-C(7B)-H(7B2)	108.5
C(2A)-C(3A)-H(3A2)	109.0	C(1B)-C(7B)-H(7B2)	108.5
H(3A1)-C(3A)-H(3A2)	107.8	H(7B1)-C(7B)-H(7B2)	107.5
N(1B)-C(4B)-C(3B)	123.81(19)	C(1A)-C(7A)-C(6A)	114.8(2)
N(1B)-C(4B)-C(5B)	115.4(2)	C(1A)-C(7A)-H(7A1)	108.6
C(3B)-C(4B)-C(5B)	120.8(2)	C(6A)-C(7A)-H(7A1)	108.6
N(1B)-C(4B)-H(4B)	90.0	C(1A)-C(7A)-H(7A2)	108.6
C(3B)-C(4B)-H(4B)	90.0	C(6A)-C(7A)-H(7A2)	108.6
C(5B)-C(4B)-H(4B)	90.0	H(7A1)-C(7A)-H(7A2)	107.5
N(3B)-C(8B)-N(2B)	116.86(19)	C(7B)-C(6B)-C(5B)	115.3(2)
N(3B)-C(8B)-S(1B)	122.70(17)	C(7B)-C(6B)-H(6B1)	108.5
N(2B)-C(8B)-S(1B)	120.45(17)	C(5B)-C(6B)-H(6B1)	108.5
C(4A)-C(5A)-C(6A)	115.81(19)	C(7B)-C(6B)-H(6B2)	108.5
C(4A)-C(5A)-H(5A1)	108.3	C(5B)-C(6B)-H(6B2)	108.5
C(6A)-C(5A)-H(5A1)	108.3	H(6B1)-C(6B)-H(6B2)	107.5
C(4A)-C(5A)-H(5A2)	108.3	C(7B)-C(1B)-C(2B)	115.4(3)
C(6A)-C(5A)-H(5A2)	108.3	C(7B)-C(1B)-H(1B1)	108.4
H(5A1)-C(5A)-H(5A2)	107.4	C(2B)-C(1B)-H(1B1)	108.4

C(1B)-C(2B)-C(3B)	115.1(3)	C(7B)-C(1B)-H(1B2)	108.4
C(1B)-C(2B)-H(2B1)	108.5	C(2B)-C(1B)-H(1B2)	108.4
C(3B)-C(2B)-H(2B1)	108.5	H(1B1)-C(1B)-H(1B2)	107.5
C(1B)-C(2B)-H(2B2)	108.5	C(1A)-C(2A)-C(3A)	114.4(2)
C(3B)-C(2B)-H(2B2)	108.5	C(1A)-C(2A)-H(2A1)	108.7
H(2B1)-C(2B)-H(2B2)	107.5	C(3A)-C(2A)-H(2A1)	108.7
C(4B)-C(5B)-C(6B)	114.4(2)	C(1A)-C(2A)-H(2A2)	108.7
C(4B)-C(5B)-H(5B1)	108.7	C(3A)-C(2A)-H(2A2)	108.7
C(6B)-C(5B)-H(5B1)	108.7	H(2A1)-C(2A)-H(2A2)	107.6
C(4B)-C(5B)-H(5B2)	108.7		
C(6B)-C(5B)-H(5B2)	108.7		
H(5B1)-C(5B)-H(5B2)	107.6		
C(4B)-C(3B)-C(2B)	117.2(2)		
C(4B)-C(3B)-H(3B1)	108.0		
C(2B)-C(3B)-H(3B1)	108.0		
C(4B)-C(3B)-H(3B2)	108.0		
C(2B)-C(3B)-H(3B2)	108.0		
H(3B1)-C(3B)-H(3B2)	107.2		
C(7A)-C(1A)-C(2A)	116.2(2)		
C(7A)-C(1A)-H(1A1)	108.2		
C(2A)-C(1A)-H(1A1)	108.2		
C(7A)-C(1A)-H(1A2)	108.2		
C(2A)-C(1A)-H(1A2)	108.2		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 2-Cycloheptylhydrazine carbothioamide. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U22	U33	U23	U13	U12	
S(1B)	84(1)	35(1)	42(1)	0(1)	-12(1)	8(1)
S(1A)	63(1)	42(1)	47(1)	3(1)	-8(1)	2(1)
N(1B)	50(1)	34(1)	40(1)	3(1)	2(1)	1(1)
N(2A)	53(1)	35(1)	41(1)	0(1)	-2(1)	0(1)
N(2B)	58(1)	33(1)	37(1)	2(1)	-1(1)	-2(1)
N(3B)	83(2)	36(1)	46(1)	4(1)	-12(1)	-6(1)
N(1A)	56(1)	33(1)	44(1)	-1(1)	1(1)	2(1)
C(6A)	53(1)	45(1)	50(1)	-6(1)	-7(1)	5(1)
C(8A)	41(1)	41(1)	37(1)	1(1)	7(1)	-3(1)
N(3A)	78(2)	41(1)	46(1)	0(1)	-10(1)	-5(1)
C(4A)	43(1)	35(1)	42(1)	3(1)	5(1)	1(1)
C(3A)	65(2)	35(1)	51(1)	0(1)	-4(1)	10(1)
C(4B)	41(1)	39(1)	39(1)	4(1)	7(1)	2(1)
C(8B)	45(1)	38(1)	36(1)	1(1)	2(1)	0(1)
C(5A)	51(1)	35(1)	44(1)	1(1)	2(1)	-1(1)
C(2B)	83(2)	52(2)	46(1)	-4(1)	-7(1)	-10(1)
C(5B)	71(2)	40(1)	48(1)	1(1)	-10(1)	13(1)
C(3B)	66(2)	40(1)	41(1)	4(1)	-1(1)	-3(1)
C(1A)	68(2)	67(2)	58(2)	26(1)	12(1)	12(1)
C(7B)	74(2)	74(2)	46(1)	17(1)	7(1)	4(1)
C(7A)	67(2)	70(2)	45(1)	11(1)	10(1)	20(1)
C(6B)	74(2)	58(2)	61(2)	24(1)	-13(1)	-14(1)
C(1B)	97(2)	74(2)	45(1)	4(1)	16(1)	19(2)
C(2A)	64(2)	44(1)	74(2)	19(1)	-13(1)	-8(1)