Thiocyanation of *closo*-Dodecaborate $[B_{12}H_{12}]^{2-}$. A Novel Synthetic Route and Theoretical Elucidation of the Reaction Mechanism. *Supporting Information*

Martin Lepšík,[§] Martin Srnec,[§] Jaromír Plešek,[≠] Bohumír Grüner,[≠] Miloš Buděšínský,[§] Blanka Klepetářová,[§] Drahomír Hnyk,[≠] and Lubomír Rulíšek[§,]*

Institute of Organic Chemistry and Biochemistry of the Academy of Sciences of the Czech Republic, Gilead Sciences Research Center, Flemingovo náměstí 2, 166 10 Prague 6, Institute of Inorganic Chemistry of the ASCR, v.v.i., No. 1001, 250 68 Husinec-Řež, Czech Republic

E-mail: lepsik@uochb.cas.cz; lubos@uochb.cas.cz.

[§] Institute of Organic Chemistry and Biochemistry of the ASCR

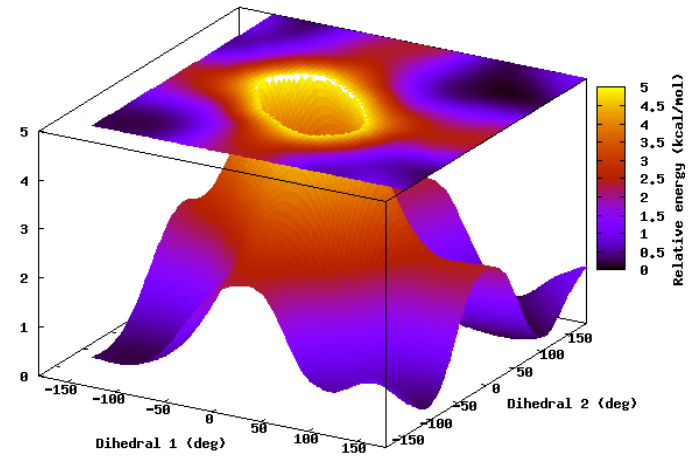
[≠] Institute of Inorganic Chemistry of the ASCR

[*] Corresponding author. Tel.: +420-220-183-263, Fax: +420-220-183-578

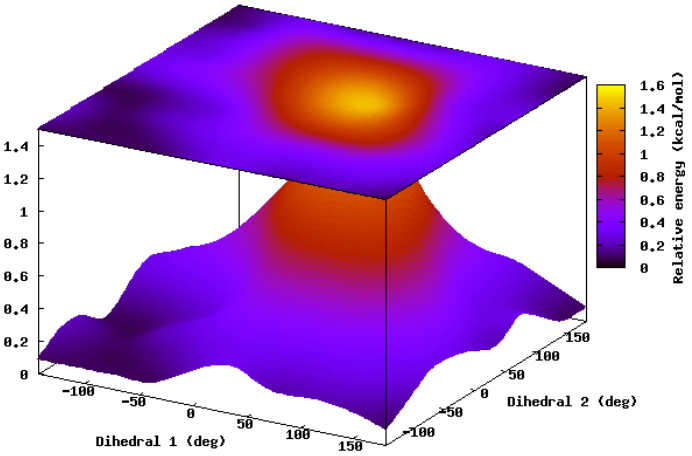
A. Calculated Thermodynamic Stabilities of All Positional Isomers of $B_{12}H_{10}(SCN)_2^{2-}$

Figure S1 shows the dependence of the relative energy (in kcal.mol^{-1}) of various rotational conformers (rotamers) of $B_{12}H_{10}(SCN)_2^{2-}$ on the values of the two scanned C-S-B-B dihedrals (Dihedral 1 and Dihedral 2) calculated for **2a** (A)**, 2b** (B) and **2c** (C). The definition of these two respective dihedrals is C1-S1-B1-B2 and C2-S2-B2-B1 for **2a,** C1-S1-B1-B2 and C7-S7-B7-B3 for **2b,** and C1-S1-B1-B2 and C12-S12-B12-B7 for **2c**.

(A)



(B)



(C)

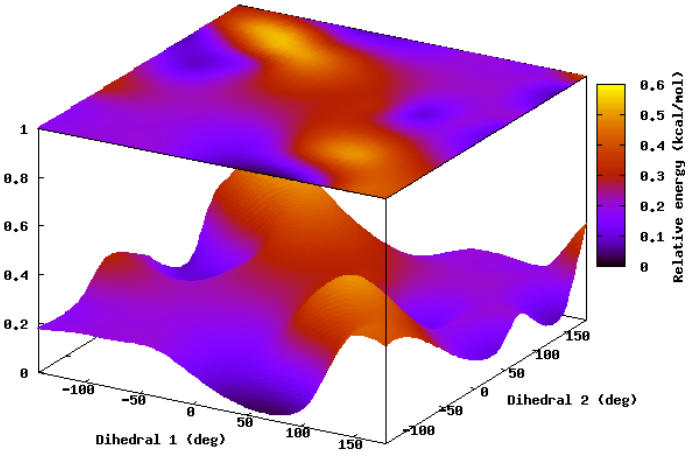


Figure S1: Potential energy surfaces of constrained 2D scan of CSBB dihedrals in $B_{12}H_{10}(SCN)_2^{2-}$

Table S1: Idealized dihedral angles of the selected rotamers of **2a**, **2b** and **2c** for unconstrained optimization. The relative energies of the optimized structures are listed.

Rotamer	Dihedral 1 (deg)	Dihedral 2 (deg)	Relative energy (kcal/mol)
2a			
1	144	144	1.6
2	72	180	1.7
3	180	108	2.4
4	**-108**	**-108**	**0.4**
2b			
1	**-108**	**-36**	**0.0**
2	180	-108	0.2
3	180	180	0.4
4	180	36	0.2
5	**-113**	**34**	**0.2**
2c			
1	-144	72	0.5
2	**36**	**-144**	**-0.4**
3	36	72	0.7

B. Mass Spectrometry and ^{11}B NMR Spectroscopic Characterization of $B_{12}H_{11}SCN^{2-}$ and $B_{12}H_{10}(SCN)_2^{2-}$

NMR spectroscopy. The ^{1}H and ^{11}B NMR spectroscopic data were recorded on a Varian Mercury 400 Plus instrument (^{1}H at 399.98 MHz; ^{11}B at 128.33 MHz) in CD_3CN and acetone-d_6 on a Bruker Avance 500 instrument (^{1}H at 500.13 MHz; ^{11}B at 160.37 MHz) in CD_3COCD_3. The NMR chemical shifts are given in ppm to high-frequency (low field) with $BF_3.OEt_2$ as the external standard. The coupling constants $^1J(^{11}B,^1H)$ are taken from the resolution-enhanced ^{11}B spectra with a digital resolution of 2 Hz and are given in Hz. The ^{11}B—^{11}B COSY spectra were used for the structural assignment of boron signals. Due to the coincidence overlaps of two signals of intensity, 2B and 4B, in the spectrum of $(Me_4N)_2$[1,7-$B_{12}H_{10}(SCN)_2$], the signals could be only tentatively assigned based on analogy with the spectra of the dihalogen derivatives of 1,7-$B_{12}H_{10}X_2^{2-}$ (Lepšík, M.; Srnec, M.; Hnyk, D.; Grüner, B.; Plešek, J.; Havlas, Z.; Rulíšek, L. *Collect. Czech. Chem. Commun.* **2009,** *74*, 1-27).

Mass Spectrometry. Mass spectrometry measurements were performed on a Thermo-Finnigan LCQ-Fleet Ion Trap instrument using electrospray (ESI) ionization. Negative ions were detected. Samples, dissolved in acetonitrile (with concentrations of approx. 100 ng.ml^{-1}), were introduced to the ion source by an infusion of 0.25 mL.h^{-1}, a source voltage of 6.0 kV, a tube lens voltage of -54.8 V, a capillary voltage of 10.0 V, while the drying temperature was 180°C, the drying gas flow 10 L min^{-1}, and auxiliary gas pressure 6 Bar. Negative ions corresponding to the molecular ion M^{2-} and $[M+X]^-$ (where X stands for an alkylammonium cation) were observed. Full agreement of the experimental and calculated isotopic distribution pattern was obtained for both of these peaks. The isotopic distribution in the boron plot of the M^{2-} peaks is in agreement with the charge, showing distances of ½ of the mass units for

dianionic compounds. The data are presented for the most abundant mass in the boron distribution plot (100%) and for the peak corresponding to the *m/z* value.

Data for $(Et_3NH)_2[B_{12}H_{11}SCN]$ (1) ^{11}B NMR: (128.33 MHz, CD_3CN, 25 ^{o}C) δ_B: -9.83 (s, 1B, B1), -14.64 (d, 5B, B2-B6, ^{1}J(B,H) = 110), -15.25 (d, 5B, B7-B11, ^{1}J(B,H) = 113), -17.16 (d, 1B, B12, ^{1}J(B,H)= 128); ^{11}B NMR {^{1}H}: (160.37 MHz, CD_3COCD_3, 25 ^{o}C) δ_B: -8.97 (s, 1B, B_1); -13.91 (s, 5B, B2-B6); -14.62 (s, 5B, B7-B11); -16.59 (s, 1B, B12).

^{1}H{^{11}B} NMR {B-H shifts from ^{1}H{$^{11}B_{sel}$} (399.98 MHz, CD_3CN, 25 ^{o}C) δ_H: 1.43 (q, 4H, 2x CH_2-N, Et_3NH^+); 1.26 (s, 5H, H2-H6); 1.23 (t, 6H, 2x CH_3, Et_3NH^+); 1.05 (s, 5H, H7-H11); 0.94 (s, 1H, H12); MS 99.67 (55%) 100.59 (12%), calcd. 100.58 M^{2-}, 301.17 (100%) 303.08 (15%), calcd. 303.30 $[M+Et_3NH]^-$.

Data for $(Me_4N)_2[1,7\text{-}B_{12}H_{10}(SCN)_2]$. (2b) ^{11}B NMR (128.33 MHz, CD_3CN, 25 ^{o}C) δ_B: -9.55 (s, 2B, B1,B7); -14.35 (d, 6B, ^{1}J(B,H) = 131, B2, B3, B4, B6, B8, B11); -15.11 (d, 2B, ^{1}J(B,H) = 104, B9,B10); -16.28 (d, 2B, B5, B12, ^{1}J(B,H) = 146);

^{11}B NMR {^{1}H}: (160.37 MHz, CD_3COCD_3, 25 ^{o}C) δ_B: -8.44 (s, 2B, B1,B7); -12.84 (s, 2B, B2,B3); -13.3 (s, 4B, B4,B6,B8,B11); -13.93 (s, 2B, B5,B12); -15.06 (s, 2B, B9,B10).

^{1}H{^{11}B} NMR, {B-H shifts from ^{1}H{$^{11}B_{sel}$} (399.983 MHz, CD_3CN, 25 ^{o}C) δ_H: 3.075 (24H, 2x Me_4N^+); 1.56 (s, 2H) and 1.35 (s, 4H) (H2,H3,H4,H6,H8,H11); 1.46 (s, 2H, H9,H10), 1.23 (s, 2H, H5,H12);

MS 128.04 (100%) 129.00 (4%), calcd. 129.07 M^{2-}, 330.33 (55%), 333.25 (12%), calcd. 333.24 $[M+Me_4N]^-$.

Table S2. ^{11}B NMR chemical shifts of **1** computed using the GIAO-HF and GIAO-MP2 methods in combination with two basis sets, def2-SVP and def2-TZVP.

	B1	B2-B6	B7-B11	B12
HF/def2-SVP	-8.3	-12.6	-13.4	-13.4
MP2/def2-SVP	-6.4	-12.2	-12.9	-15.1
HF/def2-TZVP	-10.9	-14.3	-15.1	-15.3
MP2/def2-TZVP	-9.4	-14.4	-15.3	-17.8

C. Comparison of Calculated Solvation Energies

In Table S3, we list the difference in solvation energies (in kcal/mol) between the reactants and the reactant complex calculated using eight different setups. The values range from 39.4 – 55.0 kcal/mol and thus there is some uncertainty in the calculated total free energies. However, we hope that a consistent treatment could lead to some cancellation of errors. We are also encouraged by observing that setup 1 used throughout this study has yielded virtually the same value as setup 8 which represents a "universal solvation model" of Truhlar *et al.* and should be deemed as a reference.

Table S3. ^{11}B NMR chemical shifts of **1** computed using the GIAO-HF and GIAO-MP2 methods in combination with two basis sets, def2-SVP and def2-TZVP.

Setup	1	2	3	4	5	6	7	8
Program	Turbomole			Gaussian				
Solvation model	COSMO			CPCM				SMD
QM level	PBE/def2-SVP			HF/6-31G*			B3LYP/6-311+G**	B3LYP/6-31G*
Atomic radii	Bondi* 1.17	Bondi*1.17 for boron Optimized for H,S,C,N	same as 2, except 1.2 Å - H	Bondi	Pauling	UFF	UFF	
Energy (kcal/mol)	**41.2**	**39.4**	**40.7**	**51.6 (53.7)[a]**	**53.0 (55.0)[a]**	**45.5 (46.7)[a]**	**44.0 (45.3)[a]**	**(41.0)[a]**

[a] In parenthesis there are values including non-electrostatic solvation energy terms

D. Geometries of all the relevant structures: reactants, reactant complexes, transition states, product complexes and products

First Thiocyanation (Eq. 4)
Reactant $B_{12}H_{12}^{2-}$

24
Energy = -304.9851400273
B -0.0000000 0.0000234 1.7058096
B -0.8967927 -1.2343716 0.7629342
B 0.8967927 -1.2343716 0.7629342
B 1.4509413 0.4714364 0.7627761
B 0.0000000 1.5258920 0.7629178
B -1.4509413 0.4714364 0.7627761
B -1.4509413 -0.4714364 -0.7627761
B -0.0000000 -1.5258920 -0.7629178
B 1.4509413 -0.4714364 -0.7627761
B 0.8967927 1.2343716 -0.7629342
B -0.8967927 1.2343716 -0.7629342
B 0.0000000 -0.0000234 -1.7058096
H -1.5429248 -2.1239006 1.3129506
H 1.5429248 -2.1239006 1.3129506
H 2.4969189 0.8115911 1.3123707
H -0.0000000 2.6252712 1.3129035
H -2.4969189 0.8115911 1.3123707
H -2.4969189 -0.8115911 -1.3123707
H 0.0000000 -2.6252712 -1.3129035
H 2.4969189 -0.8115911 -1.3123707
H 1.5429248 2.1239006 -1.3129506
H -1.5429248 2.1239006 -1.3129506
H -0.0000000 0.0000816 -2.9351123
H 0.0000000 -0.0000816 2.9351123

Reactant $(SCN)_2$
6
Energy = -981.0971817044
N -0.2713403 -0.3878182 0.0475640
C -0.1550272 -0.0599809 1.1740326
S -0.1021755 0.4363771 2.7970151
S 1.9146919 -0.0489756 3.3337816
C 2.7253868 1.3977680 2.9700893
N 3.3545791 2.3696257 2.7479829

Reactant Complex

30
Energy = -1286.1470426320
B -2.1561367 -1.2677617 -0.8967659
B -2.1904302 0.4858321 -1.3860290
B -3.5955922 1.2525830 -0.5757611
B -4.4100543 -0.0048341 0.3975553
B -3.7164085 -0.4349136 -1.1925499
B -3.5393681 -1.5535670 0.2093593
B -1.9010659 -1.3406464 0.9030425
B -1.1898994 -0.0712658 -0.0673744
B -1.9576944 1.4883836 0.1097121
B -1.7774570 0.3621462 1.5196528
B -3.3422923 1.1772474 1.2042297
B -3.3074193 -0.5554367 1.6904701
H -3.7061477 -0.9259537 2.7845748
H -4.1043180 -2.6366880 0.2421940
H -1.2642573 -2.2461621 1.4136944
H -1.0469525 0.6393440 2.4569554
H -3.7671120 2.0461242 1.9517802
H -5.6223952 0.0130430 0.5650040
H -4.4098549 -0.7194863 -2.1577242
H -1.7036034 -2.1239142 -1.6370704
H 0.1915313 -0.1534385 -0.2571253
H -1.3545405 2.5474294 0.0715525
H -4.2027609 2.1733923 -1.1024642
H -1.7586643 0.8477426 -2.4665419
S 1.7542785 0.1918159 -0.0419680
S 4.3041736 0.9051369 0.2442655
C 5.1129796 -0.4638325 0.7576677
N 5.7367936 -1.4032457 1.1331086
C 2.0451422 -0.1275017 -1.6836398
N 2.2501183 -0.3456258 -2.8254993

Transition State

30
Energy = -1286.2008017450
B -1.8434278 -1.3390542 -0.3641645
B -1.9324684 0.2480746 -1.2488905
B -3.2420721 1.2079987 -0.5053394
B -3.9630393 0.2288687 0.8151463
B -3.4252636 -0.5717725 -0.6943477
B -3.1006816 -1.3374146 0.9111191
B -1.4038983 -0.9968929 1.3671161
B -0.7551613 -0.0025697 0.0475998
B -1.5409280 1.5639185 -0.0682596
B -1.2157129 0.7923521 1.5508915
B -2.8040049 1.5430475 1.2049969
B -2.7189809 -0.0247516 2.0820630

H -3.0014374 -0.1203163 3.2638420
H -3.6495816 -2.3713932 1.2500843
H -0.6947300 -1.7731198 1.9807114
H -0.3893416 1.2597266 2.3094014
H -3.1459485 2.5709601 1.7642406
H -5.1467533 0.3167708 1.0957965
H -4.2054215 -1.0654077 -1.4899028
H -1.4524534 -2.3525668 -0.9227973
H 0.1283693 -1.1013337 -0.5759699
H -0.9434972 2.5627996 -0.4170314
H -3.9010981 1.9915128 -1.1661028
H -1.5895160 0.3229591 -2.4113030
S 1.3413843 -0.2721459 -0.2656667
S 4.2468478 0.7318293 -0.2300676
C 5.1181082 -0.6886927 -0.1648009
N 5.7690945 -1.6871777 -0.1120235
C 1.4710275 0.2744194 -1.8857953
N 1.5198225 0.6237678 -3.0086626

Product Complex

30
Energy = -1286.1972685340
B -1.3778125 -1.1155091 -0.5224834
B -1.9667256 0.4036706 -1.3102277
B -3.3871945 0.9846396 -0.3849147
B -3.6753493 -0.1604220 0.9619577
B -3.1304889 -0.7758105 -0.6319098
B -2.4412182 -1.4538478 0.8795457
B -0.8424744 -0.7022472 1.1441042
B -0.5973767 0.4406791 -0.1946934
B -1.7950863 1.7508354 -0.1244547
B -1.0894329 1.0698982 1.3883558
B -2.8477443 1.3962689 1.2761709
B -2.2586871 -0.1104367 2.0582676
H -2.3599829 -0.2915460 3.2644457
H -2.6733791 -2.5999077 1.2402545
H 0.0894150 -1.2894254 1.6802271
H -0.3261150 1.7261877 2.0838140
H -3.3715408 2.2942442 1.9226544
H -4.8037589 -0.3814692 1.3825562
H -3.8619812 -1.4362296 -1.3574203
H -0.8207840 -1.9886445 -1.1693425
H 2.1906934 -0.7363524 0.1619275
H -1.5212383 2.8846122 -0.4896740
H -4.3018460 1.5850655 -0.9338320
H -1.8227802 0.5889110 -2.5079586
S 1.2429356 0.8785009 -0.6738062
S 2.7074008 -1.8782337 0.8738830
C 4.3228534 -1.7305285 0.3837685

N 5.4714026 -1.6957421 0.1049113
C 1.4629295 0.4841970 -2.3101467
N 1.7116008 0.2696858 -3.4448449

Products – $B_{12}H_{11}SCN^{2-}$

26
Energy = -795.0185982751
B -0.0104001 0.0132492 1.5439033
B -1.4623134 0.4720878 0.6315877
B -0.8938003 1.2259711 -0.8897952
B 0.0077287 -0.0151288 -1.8211546
B 0.9007130 1.2264448 -0.8900544
B 1.4557435 -0.4788630 -0.8724385
B 0.0027140 -1.5351378 -0.8717310
B -1.4477824 -0.4807351 -0.8878610
B -0.9070649 -1.2370894 0.6385838
B 0.8940301 -1.2322675 0.6537321
B 1.4545310 0.4799503 0.6365601
B 0.0001868 1.5355669 0.6305449
H -1.5398183 -2.1104873 1.2162251
H 1.5270608 -2.1039075 1.2372407
H 2.4811354 0.8145697 1.2126167
H -0.0043087 2.6209736 1.1918872
H -2.4930697 0.8121372 1.1934303
H -2.4896746 -0.8221759 -1.4365563
H 0.0089318 -2.6379624 -1.4074336
H 2.5030109 -0.8259265 -1.4076536
H 1.5456220 2.1115167 -1.4407117
H -1.5369783 2.1103839 -1.4429746
H 0.0125686 -0.0231866 -3.0472888
S 0.1168620 -0.1601311 3.4772784
C -0.7832031 1.0798187 4.1864045
N -1.3759228 1.8968848 4.8074533

Products – HSCN

4
Energy = -491.1427782296
C 2.7350542 1.3941820 2.9798743
N 3.3496233 2.3705869 2.7475691
S 1.9506866 -0.0688411 3.3490980
H 0.7073314 0.3689176 2.9907483

Second Thiocyanation (Eq. 5)

TS-ortho

32
Energy = -1776.2189572140
B -1.3302780 0.7651082 1.7198462
B -2.7334498 -0.2388500 2.1521304
B -2.9582294 1.4011538 1.4334688
B -1.6752263 1.6619502 0.1891818
B -0.7369711 0.1587509 0.1515611
S 1.3931865 -0.0158067 -0.2609475
C 1.4451908 0.9682243 -1.6649281
N 1.4556219 1.6765271 -2.6044183
B -1.6859721 -1.2186593 -0.3902774
B -1.2962177 -0.9970581 1.3695088
B -2.9545111 -1.4516283 0.8523445
B -3.3278893 -0.5726109 -0.6714693
B -3.9700182 0.0263868 0.8898156
B -3.3237486 1.1899960 -0.3146988
B -1.9105440 0.4284088 -1.1187137
S 3.5053637 -1.4645084 -1.6907162
C 4.9044792 -0.8666518 -1.0033323
N 5.9230697 -0.4684961 -0.5304752
H -2.9916529 -0.4636264 3.3191423
H -3.3988630 -2.5598139 1.0905506
H -0.5288942 -1.7345313 1.9578000
H -3.3754688 2.3366538 2.0863874
H -5.1584700 -0.0206386 1.1518152
H -4.0505697 -1.0502333 -1.5269544
H -1.1817101 -2.1235390 -1.0220988
H 0.5640318 0.9962735 0.4432019
H -1.1681571 2.7450280 -0.0179922
H -4.0392350 1.9732534 -0.9106801
H -1.5749750 0.6682367 -2.2593805
S -0.0876716 1.3913220 3.0474168
C -0.4213362 3.0474636 3.1709795
N -0.5839986 4.2046600 3.3452460

TS-meta

32
Energy = -1776.2224728160
B -1.2384886 -0.4504294 -0.6564036
B -0.7920565 1.1383130 -1.4046703
B -1.8919275 2.3886734 -0.7500319
B -3.0216970 1.5922748 0.3843318
B -2.5129456 0.7365752 -1.1101332
B -2.6012216 -0.1427110 0.4448679
B -0.9626008 -0.3208638 1.1370966
B 0.0913879 0.5207315 -0.0027725
B -0.2377632 2.2432549 -0.0793035
B -0.3540055 1.3391356 1.4957146
B -1.6259949 2.5115361 1.0229246
B -2.0757057 0.9379219 1.7688355
H -2.5502790 0.8449311 2.8854182
S -3.9278299 -1.4645002 0.8935787
H -0.6070110 -1.2944685 1.7702783
H 0.4453876 1.5270469 2.3889840
H -1.7612467 3.5607082 1.6251844
H -4.1720705 1.9563624 0.5333437
H -3.2844285 0.4917855 -2.0139078
H -1.0746712 -1.5070575 -1.2363179
H 0.8308817 -0.6982133 -0.6529141
H 0.6414857 3.0574436 -0.2704638
H -2.2223808 3.3490455 -1.4202555
H -0.2877116 1.1744174 -2.5070380
S 2.1078493 -0.2215383 -0.0519345
S 4.9952877 0.1558085 0.5633557
C 5.4721425 -1.4437004 0.5621869
N 5.8409299 -2.5770594 0.5731447
C 2.6088848 0.4716797 -1.5395567
N 2.9061987 0.9323158 -2.5806923
C -4.4545870 -2.0701116 -0.5949897
N -4.8944196 -2.5616931 -1.5765591

TS-para

32
Energy = -1776.2234466440
B -1.8609605 -1.3462333 -0.3583441
B -1.9302817 0.2338159 -1.2534216
B -3.2310179 1.2142907 -0.5212448
B -3.9292595 0.2526270 0.8077847
B -3.4271266 -0.5677462 -0.6991382
B -3.1108218 -1.3239966 0.9203655
B -1.4096211 -0.9949825 1.3693995
B -0.7553588 -0.0187510 0.0427320
B -1.5317403 1.5560065 -0.0808925
B -1.2053347 0.7936670 1.5414616
B -2.7863583 1.5598856 1.1981348
B -2.7041161 -0.0058841 2.0871115
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H 0.1596012 -1.1013468 -0.6043164
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H -3.9038935 1.9925237 -1.1653991
H -1.5911441 0.3003729 -2.4161007
S 1.3452147 -0.2665803 -0.2535619
S 4.1524665 0.7721320 -0.1653052
C 4.9816982 -0.6761820 -0.1500109
N 5.6012705 -1.6945362 -0.1326893
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