Supporting Information

What is the preferred geometry of sulfur–disulfide interactions?

Ivana S. Veljković,[a] Dušan Ž. Veljković,[b] Gordana G. Sarić,[b] Ivana M. Stanković,[a] Snežana D. Zarić[b*]

[a] Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia

[b] University of Belgrade - Faculty of Chemistry, Studentski trg 12−16, 11000 Belgrade, Serbia

CAMBRIDGE STRUCTURAL DATABASE SEARCH DETAILS

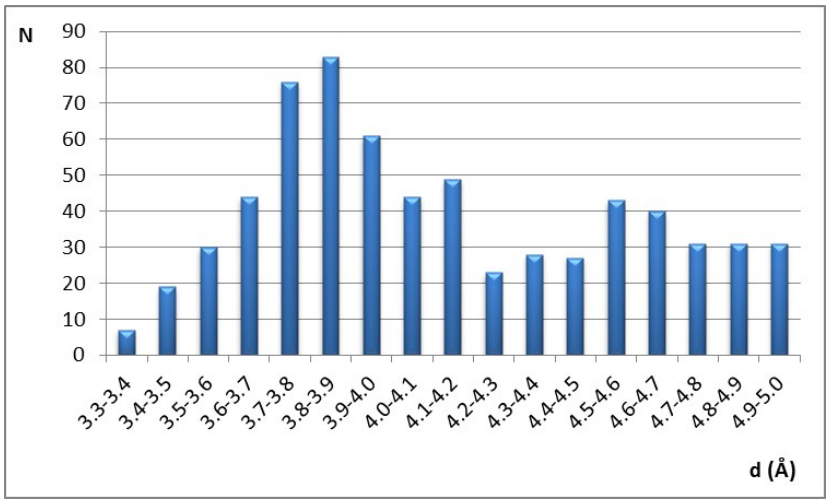
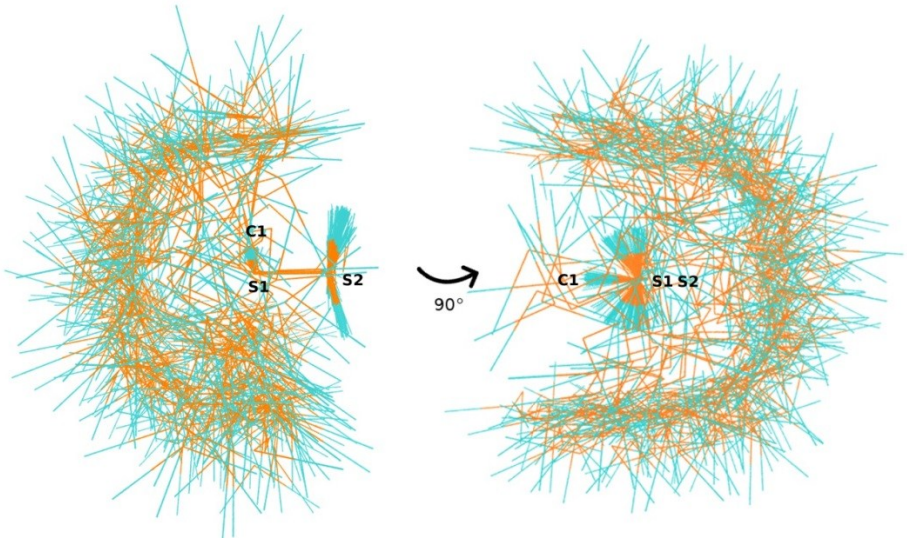


Figure S1. Distribution of distance d

To visualize preferred orientations of interacting molecules, we have structurally aligned all the disulfide bonds interacting with sulfur that were found in CSD. In that arrangement all the sulfurs form a cloud around aligned disulfide bonds. In each structure, atom S_1 (the sulfur from the disulfide that is closer to the sulfur from the interacting residue) was translated to the coordinate system origin, atom S_2 is put in the x-axis, and C_1 atom (the atom bound to the S_1) is put in the x-y plane. In this way, all the sulfur atoms (S_3) interacting with the aligned disulfide group form a cloud around the disulfide group. The coordinate transformations were done in Python language, and the visualizations in VMD software.

The alignment of all disulfide groups found in CSD was performed and visualized (Figure S4). It is visible that the interactions represent a variety of geometries. As can be noticed from Figure S4B, in some parts there is a lower density (with α angle of 160-180° degrees of contacts indicating a smaller number of contacts at the values of mentioned angle. Also, it is very clear that there are no contacts when α value is about 0° in the region around sulfur atom labeled as S_2.



A. **B.**

Figure S2. A. All the disulfide/sulfur interactions found in CSD are structurally aligned. The reference group for the alignment is the disulfide bond, and the C-S_3-C group forms a cloud around it. **B.** Another view of the same image obtained by rotation for 90°. Sulfur atoms are represented in orange and carbon atoms in cyan.

VIBRATIONAL FREQUENCIES CALCULATIONS

Structures of dimethyl sulfide and dimethyl disulfide were optimized using MP2 method and cc-pVTZ basis set. Vibrational frequencies for optimized geometries of both monomers (Tables S1 and S2) have only positive values, which confirms that optimized geometries are correct.

Table S1. Vibrational frequencies and intensities of IR spectrum of dimethyl sulfide molecule

Frequencies (cm^{-1})	Intensities
181.21	0.0000
192.95	0.9335
263.62	0.0394
726.46	2.5502
779.28	0.0061
921.79	0.3474
963.41	0.0000
999.12	4.5818
1057.02	9.6652
1347.31	5.3710
1371.89	0.4197
1478.37	0.0000
1487.81	14.3575
1494.73	15.0486
1502.92	0.2636
3070.35	27.3881
3075.65	23.9978
3161.85	22.0096
3170.64	0.0001
3186.04	8.3349
3187.37	1.8823

Table S2. Vibrational frequencies and intensities of IR spectrum of dimethyl disulfide molecule

Frequencies (cm^{-1})	Intensities
99.75	1.1241
153.65	0.0066
166.94	0.2539
236.20	1.0069
266.48	0.8229
532.48	0.4134
724.74	2.2101
728.03	0.0065
973.33	1.6835
974.48	1.1246
981.50	12.3560
983.18	2.0459
1343.07	5.8020
1351.21	0.5176
1471.02	9.7745
1477.04	6.5473
1489.36	0.4232
1493.59	13.8960
3078.09	18.6999
3079.30	15.6191
3179.32	5.0065
3179.71	3.2779
3195.18	4.9449
3195.36	2.8349

Table S3. Comparison of interaction energies in model systems A - D calculated at MP2/cc-PVQZ and CCSD(T)/CBS levels of theory. All energies are given in kcal/mol.

Model system	$\Delta E_{MP2/cc\text{-}PVQZ}$	$\Delta E_{CCSD(T)/CBS}$
A_{NB1}	-1.22	-1.20
A_B	-1.61	-1.54
A_{NB2}	-0.64	-0.69
A_{NB3}	-1.47	-1.50
A_{NB4}	-1.86	-1.88
B_{NB1}	-0.73	-0.77
B_{NB2}	-0.43	-0.49
C_{NB1}	-2.65	-2.55
C_B	-2.96	-2.83
C_{NB2}	-1.65	-1.66
C_{NB3}	-2.49	-2.47
C_{NB4}	-3.33	-3.26
D_{NB1}	-2.04	-1.98
D_B	-2.53	-2.43
D_{NB2}	-2.50	-2.42
D_{NB3}	-2.61	-2.54
D_{NB4}	-2.70	-2.68

ENERGIES OF S-S···S INTERACTIONS FOR DIFFERENT ORIENTATION OF DIMETHYL DISULFIDE AND DIMETHYL SULFIDE MOLECULES

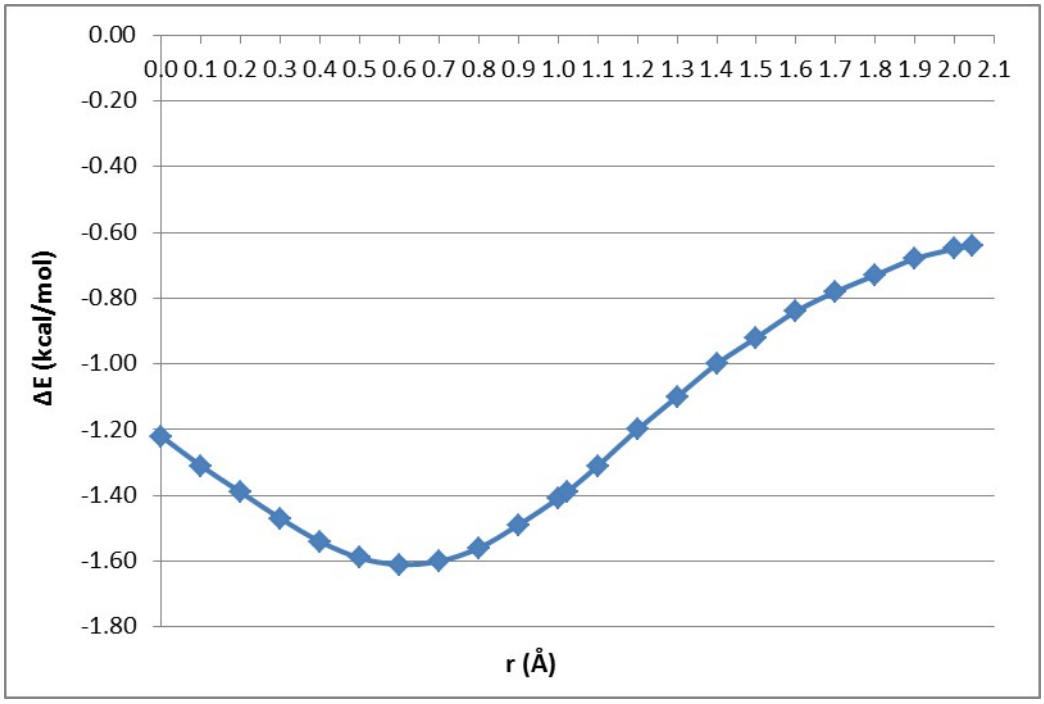


Figure S3. Potetial energy curve for model system A within region 2 (Figure 5, Main text) calculated at MP2/ cc-pVQZ level. The curve was obtained by changing the normal distances (*R*) for a series of offsets (*r*) and present the energies of the strongest interaction for each offset.

Table S4. Interaction energies for model system A within regions 1 and 3 (Figure 6, main text)

Region around S1 atom			**Region around S2 atom**		
angle α (°)	$S_1 \cdots S_3$ distance (Å)	ΔE (kcal/mol)	angle α (°)	$S_2 \cdots S_3$ distance (Å)	ΔE (kcal/mol)
100	3.70	-0.70	100	4.00	-0.49
110	3.90	-0.39	110	4.00	-0.48
120	3.90	-0.24	120	4.00	-0.58
130	4.00	-0.21	130	3.90	-0.79
140	4.00	-0.27	140	3.80	-1.08
150	3.90	-0.43	150	3.70	-1.40
160	3.80	-0.73	160	3.70	-1.66
170	3.60	-1.17	170	3.70	-1.83
180	3.70	-1.47	180	3.70	-1.86

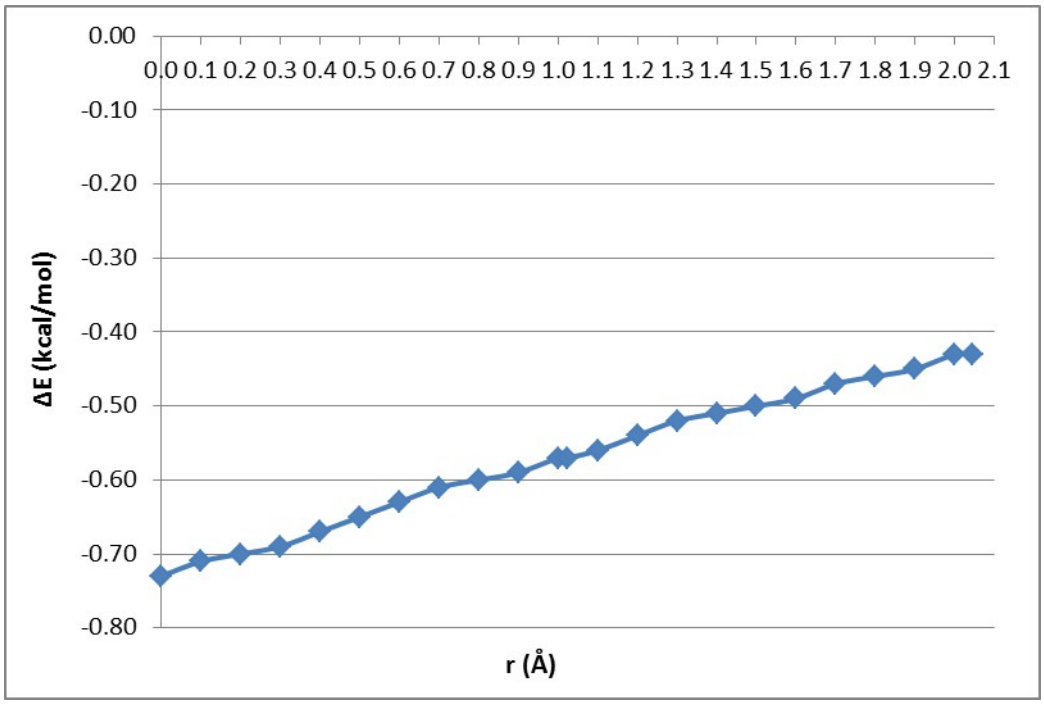


Figure S4. Potetial energy curve for model system B within region 2 (Figure 5, Main text) calculated at MP2/ cc-pVQZ level. The curve was obtained by changing the normal distances (*R*) for a series of offsets (*r*) and present the energies of the strongest interaction for each offset.

Table S5. Interaction energies for model system B within regions 1 and 3 (Figure 6, main text)

Region around S1 atom			**Region around S2 atom**		
angle α (°)	$S_1 \cdots S_3$ distance (Å)	ΔE (kcal/mol)	angle α (°)	$S_2 \cdots S_3$ distance (Å)	ΔE (kcal/mol)
100	3.70	-0.67	100	4.00	-0.35
110	3.70	-0.59	110	4.00	-0.39
120	3.70	-0.55	120	3.90	-0.51
130	3.70	-0.59	130	3.80	-0.70
140	3.70	-0.73	140	3.80	-1.94
150	3.60	-0.99	150	3.70	-1.19
160	3.60	-1.37	160	3.70	-1.36
170	3.50	-1.77	170	3.70	-1.44
180	3.70	-1.86	180	3.70	-1.47

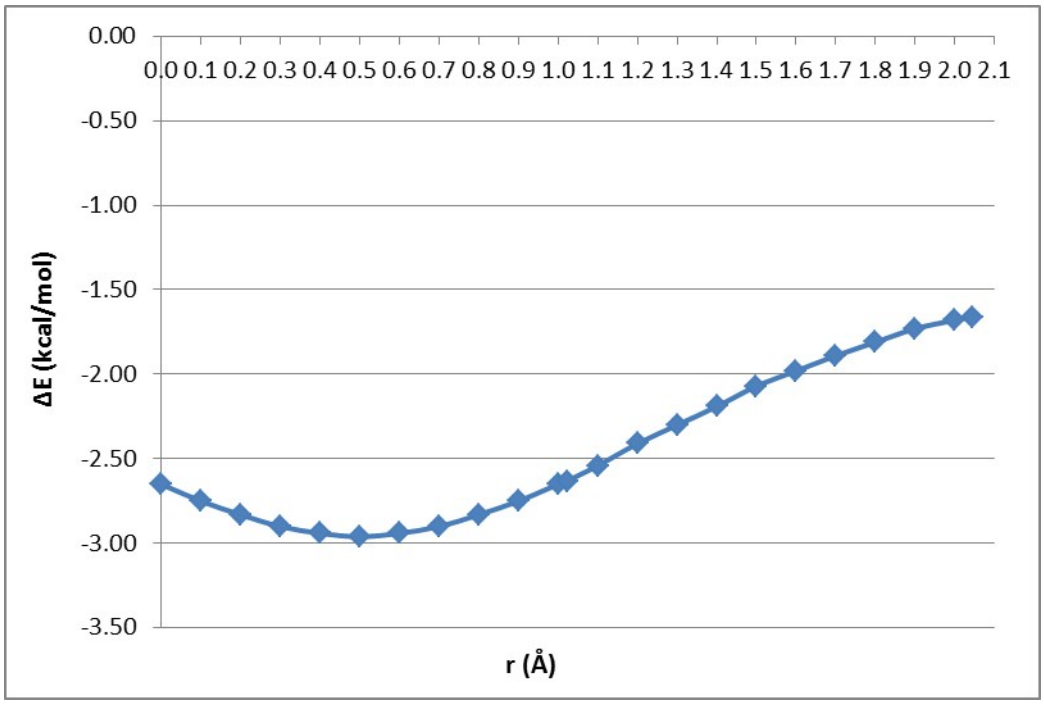


Figure S5. Potetial energy curve for model system C within region 2 (Figure 5, Main text) calculated at MP2/ cc-pVQZ level. The curve was obtained by changing the normal distances (*R*) for a series of offsets (*r*) and present the energies of the strongest interaction for each offset.

Table S6. Interaction energies for model system C within regions 1 and 3 (Figure 6, main text)

Region around S1 atom			**Region around S2 atom**		
angle α (°)	$S_1 \cdots S_3$ distance (Å)	ΔE (kcal/mol)	angle α (°)	$S_2 \cdots S_3$ distance (Å)	ΔE (kcal/mol)
100	3.60	-2.06	100	3.90	-1.49
110	3.70	-1.51	110	3.90	-1.46
120	3.80	-1.19	120	3.80	-1.63
130	3.80	-1.09	130	3.70	-1.98
140	3.80	-1.18	140	3.60	-2.43
150	3.70	-1.49	150	3.60	-2.88
160	3.60	-2.03	160	3.60	-3.19
170	3.60	-2.49	170	3.60	-3.33
180	3.80	-2.38	180	3.60	-3.31

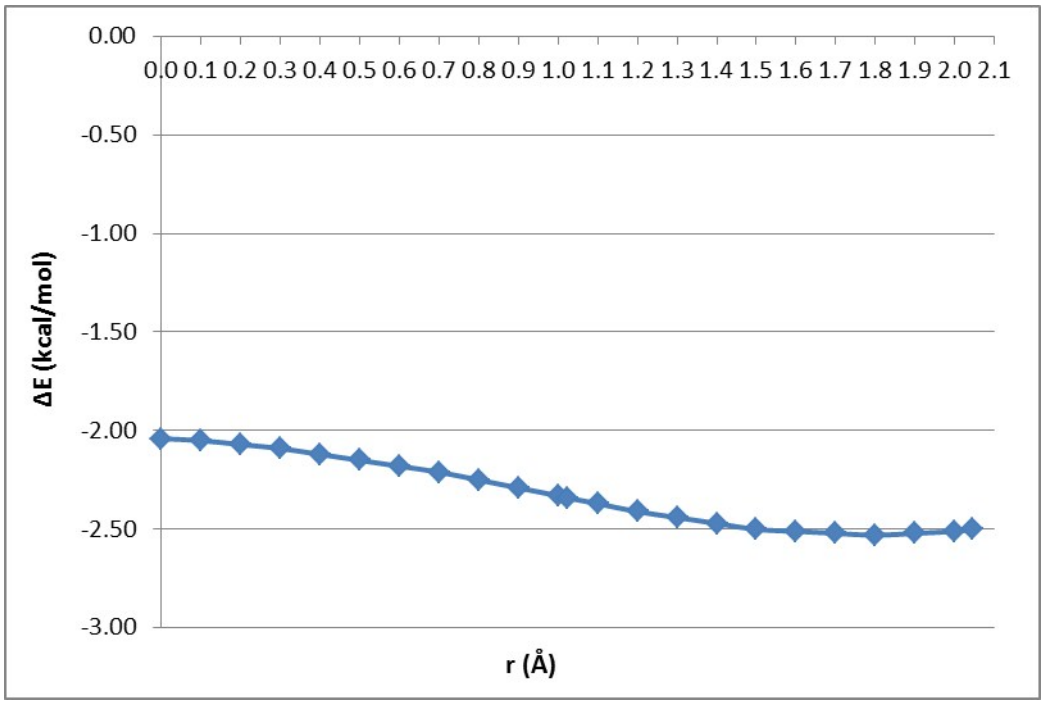


Figure S6. Potetial energy curve for model system D within region 2 (Figure 5, Main text) calculated at MP2/ cc-pVQZ level. The curve was obtained by changing the normal distances (*R*) for a series of offsets (*r*) and present the energies of the strongest interaction for each offset.

Table S7. Interaction energies for model system D within regions 1 and 3 (Figure 6, main text)

Region around S1 atom			**Region around S2 atom**		
angle α (°)	$S_1 \cdots S_3$ distance (Å)	ΔE (kcal/mol)	angle α (°)	$S_2 \cdots S_3$ distance (Å)	ΔE (kcal/mol)
100	3.60	-1.89	100	3.60	-2.35
110	3.60	-1.77	110	3.60	-2.31
120	3.60	-1.70	120	3.60	-2.35
130	3.60	-1.70	130	3.60	-2.45
140	3.60	-1.78	140	3.60	-2.57
150	3.60	-1.95	150	3.60	-2.66
160	3.50	-2.23	160	3.60	-2.70
170	3.50	-2.54	170	3.60	-2.68
180	3.65	-2.61	180	3.70	-2.67

DETAILS OF ENERGY DECOMPOSITION ANALYSIS

The correlation between the interaction energies and electrostatic component computed by SAPT 2+3 method for all studied model systems is presented in Figure S8. Almost a linear relationship can be noticed with a correlation coefficient R^2 of 0.8934. This results demonstrate high importance of electrostatic component for the strenght and geometry of the S-S···S interaction.

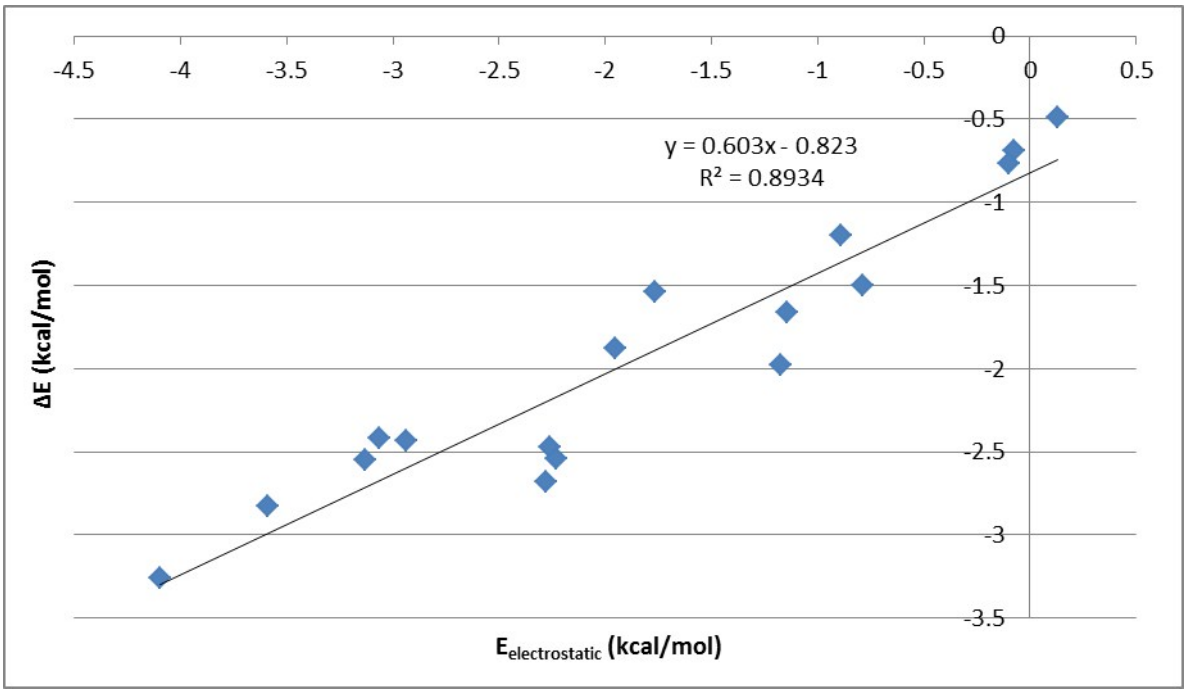


Figure S7. Electrostatic component value versus interaction energy

CARTESIAN COORDINATES OF MODEL SYSTEMS

A_{NB1} geometry

S	-1.717681	0.974748	-0.595502
S	-1.285748	-0.951629	-0.062088
C	-2.936962	-1.697437	0.002952
H	-2.791232	-2.74831	0.248615
H	-3.542969	-1.23143	0.775714
H	-3.425802	-1.61227	-0.96306
C	-2.076854	1.733134	1.011612
H	-2.283015	2.784626	0.817233
H	-2.950478	1.276507	1.469697
H	-1.216789	1.645724	1.668913
S	2.125181	-0.169537	0.000364
C	3.566158	-1.187592	0.376613
C	2.991024	1.37745	-0.333647
H	4.101772	-0.796044	1.238908
H	4.235923	-1.241416	-0.479111
H	3.208798	-2.187768	0.607936
H	2.242079	2.123719	-0.586101
H	3.673977	1.264918	-1.173085
H	3.539501	1.711087	0.544763

A_{B} geometry

S	-1.471977	0.991954	-0.590529
S	-1.360609	-0.973411	-0.036487
C	-3.108282	-1.455616	-0.027261
H	-3.134746	-2.514301	0.226525
H	-3.66134	-0.89543	0.722331
H	-3.544779	-1.304322	-1.010102
C	-1.764814	1.810025	1.000689
H	-1.799684	2.879053	0.796031
H	-2.713545	1.497157	1.429167
H	-0.951519	1.596792	1.68806
S	1.993645	-0.155589	-0.024281
C	3.246771	-1.38011	0.405416
C	3.09848	1.236845	-0.332311
H	3.806475	-1.068455	1.284816
H	3.92915	-1.543548	-0.426083
H	2.73183	-2.311392	0.627044
H	2.482583	2.087353	-0.613161
H	3.784278	1.013509	-1.146895
H	3.66141	1.489437	0.563821

A_{NB2} geometry

S	-1.392656	0.892562	-0.572302
S	-1.945345	-0.985834	0.017773
C	-3.752277	-0.894462	-0.098909
H	-4.1288	-1.880868	0.16784
H	-4.149437	-0.160865	0.597991
H	-4.051208	-0.651397	-1.114269
C	-1.518958	1.821227	0.979664
H	-1.200535	2.838567	0.757072
H	-2.544604	1.838488	1.339277
H	-0.863017	1.389882	1.730051
S	2.358009	-0.056613	-0.080793
C	3.128258	-1.595234	0.461217
C	3.864184	0.905919	-0.324489
H	3.696982	-1.441705	1.375944
H	3.778636	-1.996141	-0.313397
H	2.331839	-2.308693	0.656822
H	3.56885	1.895394	-0.664027
H	4.497737	0.447758	-1.081087
H	4.416177	1.00304	0.608043

A_{NB3} geometry

S	3.163339	-0.239742	-0.5378
S	1.128094	-0.207335	-0.340952
C	0.811002	1.555141	-0.05793
H	-0.269455	1.665083	0.022349
H	1.273003	1.888687	0.867743
H	1.176875	2.141748	-0.895442
C	3.701628	-0.345496	1.190214
H	4.788791	-0.405858	1.171408
H	3.402518	0.540236	1.744813
H	3.294976	-1.238053	1.656447
S	-2.554258	-0.148702	0.015204
C	-3.703325	1.22922	0.203333
C	-3.760962	-1.489114	0.054924
H	-3.118813	2.145677	0.198858
H	-4.241091	1.158292	1.146477
H	-4.411151	1.258219	-0.622431
H	-3.215711	-2.423511	-0.050779
H	-4.297302	-1.498683	1.001493
H	-4.467492	-1.397888	-0.767413

A_{NB4} geometry

S	-1.12673	-0.290799	-0.279132
S	-3.160949	-0.486563	-0.354325
C	-3.708424	1.216734	-0.061033
H	-4.795661	1.206021	-0.122041
H	-3.410212	1.555232	0.927935
H	-3.30603	1.877082	-0.823539
C	-0.807342	-0.41718	1.501033
H	0.272988	-0.359325	1.625383
H	-1.273349	0.404867	2.038289
H	-1.167558	-1.368737	1.880741
S	2.553765	0.063395	-0.143087
C	3.865362	-1.172847	-0.219475
C	3.59675	1.526232	0.020336
H	2.940679	2.39082	0.080565
H	4.246914	1.636253	-0.84507
H	4.196288	1.474406	0.926764
H	4.509352	-1.001038	-1.079418
H	4.458955	-1.163722	0.692286
H	3.392178	-2.146029	-0.322348

B_{NB1} geometry

S	-2.857928	-0.024298	-0.808217
S	-1.008757	-0.370906	-0.006684
C	-1.409955	-1.436974	1.403815
C	-3.434600	1.380099	0.182787
S	0.526641	1.720698	-2.644438
C	1.154924	1.290630	-4.279894
C	0.880621	3.488863	-2.696474
H	-0.462023	-1.700682	1.870510
H	-2.027992	-0.909146	2.125617
H	-1.912572	-2.337332	1.063042
H	-4.411966	1.654856	-0.211149
H	-3.536343	1.101454	1.228528
H	-2.751469	2.218066	0.080121
H	1.013248	0.221287	-4.414073
H	2.215825	1.518662	-4.358863
H	0.606111	1.819453	-5.056355
H	1.947815	3.666554	-2.811663
H	0.338126	3.968113	-3.508731
H	0.552013	3.916288	-1.752602

B_{NB2} geometry

S	-1.105901	-0.070884	-0.530307
S	-2.622275	-0.536753	0.760275
C	-4.086913	-0.243189	-0.267162
C	-0.981196	1.725919	-0.323149
S	1.508604	-0.901620	2.241739
C	2.264594	0.139864	3.505942
C	2.339459	-2.447309	2.66
H	-4.949534	-0.506627	0.343090
H	-4.157797	0.803535	-0.551614
H	-4.058154	-0.873656	-1.150949
H	-0.158862	2.053161	-0.957658
H	-1.896422	2.217872	-0.642387
H	-0.762477	1.970475	0.712104
H	1.858976	1.141678	3.390131
H	3.344467	0.179586	3.379289
H	2.024155	-0.225167	4.502278
H	3.417621	-2.348350	2.552678
H	2.097473	-2.753939	3.675462
H	1.984682	-3.207095	1.968315

C_{NB1} geometry

S	-1.390221	-0.877486	0.595070
S	-0.700655	0.932525	-0.060968
C	-2.154679	1.989997	0.172559
H	-1.856187	2.994539	-0.123614
H	-2.977798	1.662437	-0.457320
H	-2.454818	1.990648	1.216261
C	-2.194395	-1.529758	-0.893155
H	-2.561012	-2.522344	-0.635692
H	-3.033348	-0.904092	-1.186873
H	-1.477299	-1.605308	-1.705227
S	2.413495	-0.505832	-0.756091
C	2.318457	-1.452662	0.777330
C	3.236980	0.958325	-0.096531
H	1.831577	-2.397318	0.548981
H	1.729056	-0.923086	1.522916
H	3.312966	-1.654194	1.169860
H	3.375441	1.654598	-0.919697
H	2.626733	1.433489	0.668689
H	4.210448	0.701623	0.316030

C_B geometry

S	-1.567485	-0.947472	0.603086
S	-1.377379	0.975774	-0.065503
C	-3.066761	1.604476	0.128635
H	-3.043712	2.649754	-0.175968
H	-3.758456	1.062019	-0.510793
H	-3.377023	1.533073	1.16692
C	-2.136209	-1.804771	-0.88975
H	-2.227289	-2.85721	-0.62518
H	-3.10648	-1.43069	-1.206302
H	-1.408983	-1.691239	-1.68828
S	2.655825	-0.157168	-0.648349
C	2.788154	-1.081629	0.895918
C	3.041382	1.48019	0.005337
H	2.578188	-2.124403	0.672075
H	2.063038	-0.724097	1.624012
H	3.792068	-1.004534	1.308177
H	3.003948	2.181053	-0.824699
H	2.310441	1.779873	0.75344
H	4.039479	1.498658	0.43801

C_{NB2} geometry

S	0.732937	0.819626	0.568096
S	1.544993	-0.893297	-0.199032
C	3.276414	-0.746811	0.318358
H	3.778209	-1.650487	-0.024414
H	3.746880	0.118455	-0.141582
H	3.340716	-0.681073	1.400458
C	1.098200	2.021329	-0.739369
H	0.659603	2.965983	-0.421276
H	2.170860	2.148462	-0.861053
H	0.646713	1.706726	-1.675627
S	-2.703818	-0.171861	-0.856043
C	-3.497127	0.398584	0.661242
C	-2.415446	-1.883080	-0.360595
H	-3.744530	1.448430	0.526396
H	-2.823547	0.301001	1.510072
H	-4.412393	-0.157849	0.852069
H	-1.926779	-2.386262	-1.191005
H	-1.766181	-1.929081	0.511233
H	-3.355453	-2.387292	-0.146347

C_{NB3} geometry

S	2.776795	-0.379656	-0.628974
S	0.814264	-0.086875	-0.134226
C	0.714385	1.722178	-0.06851
H	-0.322821	1.965781	0.156842
H	1.352353	2.117638	0.717732
H	0.989715	2.148602	-1.028589
C	3.581467	-0.321249	0.994621
H	4.640062	-0.508806	0.821073
H	3.462331	0.657685	1.451856
H	3.176067	-1.092535	1.642822
S	-2.678219	-0.197838	0.731941
C	-2.930288	-1.532417	-0.455399
C	-2.997356	1.188627	-0.377239
H	-2.769951	-2.471197	0.068578
H	-2.218853	-1.460009	-1.275376
H	-3.945439	-1.515498	-0.846456
H	-2.284354	1.198744	-1.198987
H	-4.010939	1.144123	-0.770195
H	-2.88286	2.10255	0.199999

C_{NB4} geometry

S	-0.811572	-0.113076	-0.104314
S	-2.768748	-0.481239	-0.569013
C	-3.566588	1.067555	-0.067357
H	-4.621393	0.96654	-0.318562
H	-3.468737	1.225179	1.003693
H	-3.139411	1.903865	-0.612795
C	-0.755022	-0.566962	1.65004
H	0.277327	-0.433497	1.969983
H	-1.398404	0.081178	2.239568
H	-1.045266	-1.605485	1.778974
S	2.73753	-0.043887	0.494924
C	2.838541	1.577021	-0.290488
C	3.005603	-1.052896	-0.976284
H	2.692624	2.325605	0.484043
H	2.060856	1.691376	-1.042733
H	3.815474	1.725994	-0.74563
H	2.224063	-0.878343	-1.71281
H	3.978697	-0.844523	-1.41607
H	2.973612	-2.09497	-0.668669

D_{NB1} geometry

S	1.649549	0.804229	0.834018
S	1.249195	-0.848111	-0.30243
C	2.893103	-1.595952	-0.461385
H	2.760267	-2.514466	-1.031128
H	3.56874	-0.936717	-1.00036
H	3.295914	-1.829429	0.519751
C	2.155195	2.006847	-0.424951
H	2.352737	2.939575	0.101278
H	3.061629	1.68249	-0.929666
H	1.355466	2.156441	-1.144292
S	-2.232755	0.061233	-0.39793
C	-3.977599	0.516915	-0.445786
H	-4.126373	1.151345	-1.315805
C	-2.278795	-0.952361	1.093689
H	-4.257024	1.071734	0.447434
H	-4.605485	-0.366433	-0.541709
H	-1.270919	-1.31848	1.271769
H	-2.945103	-1.802497	0.963131
H	-2.597084	-0.363879	1.951666

D_{B} geometry

S	1.163833	0.644488	0.786559
S	1.629756	-0.882254	-0.49172
C	3.425405	-1.010678	-0.276964
H	3.752793	-1.837568	-0.905447
H	3.921019	-0.09899	-0.600631
H	3.66527	-1.223018	0.760713
C	1.465463	2.101216	-0.249748
H	1.201199	2.968688	0.353225
H	2.51341	2.167322	-0.53083
H	0.838306	2.068373	-1.135746
S	-2.155099	0.168969	-0.247171
C	-3.894542	0.01815	-0.70105
H	-4.069525	0.674964	-1.54931
C	-2.155429	-0.988448	1.136593
H	-4.536897	0.325444	0.121564
H	-4.131367	-1.003404	-0.991027
H	-1.14624	-1.017144	1.539437
H	-2.431619	-1.987279	0.805231
H	-2.837584	-0.658076	1.917146

D_{NB2} geometry

S	1.137448	0.60336	0.774727
S	1.708039	-0.875156	-0.517729
C	3.499638	-0.933851	-0.246256
H	3.881551	-1.732886	-0.879981
H	3.966713	0.004244	-0.535025
H	3.714624	-1.158235	0.794334
C	1.410903	2.093125	-0.221662
H	1.091144	2.935851	0.389474
H	2.463668	2.20846	-0.466516
H	0.814573	2.053349	-1.128416
S	-2.191892	0.190475	-0.222784
C	-3.907928	-0.022337	-0.736929
H	-4.082893	0.644671	-1.577201
C	-2.188241	-0.995285	1.136766
H	-4.58881	0.240503	0.069953
H	-4.092177	-1.046369	-1.054977
H	-1.192252	-0.99087	1.572145
H	-2.411421	-1.99736	0.776516
H	-2.908479	-0.710137	1.900764

D_{NB3} geometry

S	3.373238	0.804229	-1.396872
S	2.236790	-0.848111	-0.996518
C	2.077835	-1.595952	-2.640426
C	2.114269	2.006847	-1.902518
S	0.208411	-3.797275	-0.281950
C	-0.794109	-5.254891	0.071223
C	1.832350	-4.545110	-0.041138
H	1.508092	-2.514466	-2.507590
H	1.538860	-0.936717	-3.316063
H	3.058971	-1.829429	-3.043237
H	2.640498	2.939575	-2.100060
H	1.609554	1.682490	-2.808952
H	1.394928	2.156441	-1.102789
H	-1.837297	-4.967515	-0.032440
H	-0.623715	-5.604495	1.087338
H	-0.576496	-6.054098	-0.634227
H	2.577475	-3.774502	-0.221480
H	1.990698	-5.360427	-0.743939
H	1.942611	-4.910932	0.977568

D_{NB4} geometry

S	0.983398	-0.085596	0.007139
S	2.894941	-0.330376	-0.677047
C	3.852006	-0.252215	0.860771
C	0.84614	1.720453	0.086594
H	4.893113	-0.412595	0.584551
H	3.753854	0.723542	1.329635
H	3.530437	-1.033308	1.543326
H	-0.170219	1.938497	0.411237
H	1.5476	2.131647	0.808011
H	1.016273	2.153701	-0.894601
S	-2.602298	0.234307	-0.014054
C	-4.399128	0.394615	-0.024674
C	-2.511193	-1.557209	0.177214
H	-4.632816	1.450325	-0.136186
H	-4.824923	0.035781	0.910035
H	-4.831265	-0.152575	-0.859889
H	-1.459421	-1.83048	0.202984
H	-2.986034	-2.06041	-0.662464
H	-2.980187	-1.871342	1.107326