

## Supporting Information

### Describing the Disulfide Bond: From the Density Functional Theory and Back through the "Lego Brick" Approach

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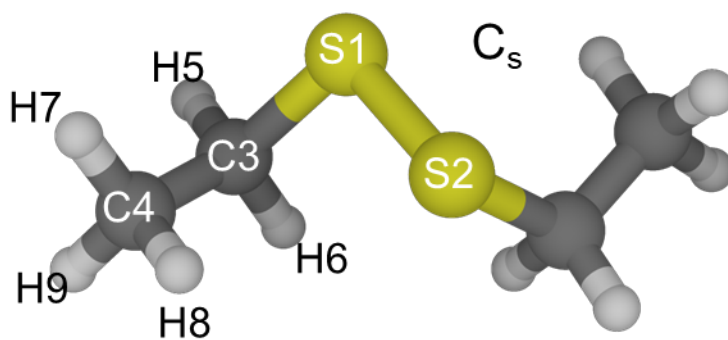
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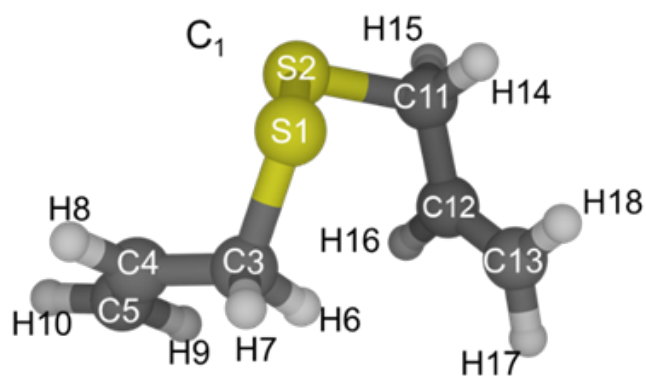
**Table S1.** revDSD and TM(+LR) parameters for diethyl disulfide ( $C_2H_5)_2S_2$ , bonds in Å, angles in degrees.

	revDSD	TM (+LR)
<i>S1S2</i>	2.0429	2.0333
<i>C3S1</i>	1.8243	1.8243 (1.8187)
<i>C4C3</i>	1.5201	1.5172
<i>H5C3</i>	1.0943	1.0911
<i>H6C3</i>	1.0917	1.0885
<i>H8C4</i>	1.0912	1.0880
<i>H7C4</i>	1.0912	1.0880
<i>H9C4</i>	1.0933	1.0901
<i>C3S1S2</i>	102.76	
<i>C4C3S1</i>	113.63	
<i>H5C3S1</i>	103.73	
<i>H6C3S1</i>	108.41	
<i>H8C4C3</i>	110.45	
<i>H7C4C3</i>	110.72	
<i>H9C4C3</i>	110.36	
<i>C3C2C1C3b</i>	67.43	
<i>C4C3S1S2</i>	87.24	
<i>H5C3S1S2</i>	-171.48	
<i>H6C3S1S2</i>	-57.39	
<i>H8C5C3S1</i>	-60.46	
<i>H7C4C3S1</i>	-59.59	
<i>H9C5C3S1</i>	179.88	



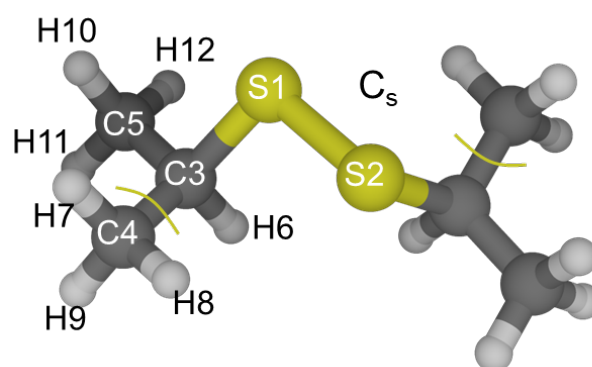
**Table S2.** revDSD and TM(+LR) parameters for diallyl disulfide (C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>S<sub>2</sub>, bonds in Å, angles in degrees.

	revDSD	TM (+LR)
<i>S1S2</i>	2.0364	2.0268
<i>S2C11</i>	1.8351	1.8351 (1.8294)
<i>C11C12</i>	1.4906	1.4879
<i>C12C13</i>	1.3345	1.3327
<i>C11H14</i>	1.0904	1.0874
<i>C11H15</i>	1.0947	1.0917
<i>C12H16</i>	1.0867	1.0837
<i>C13H18</i>	1.0843	1.0813
<i>C13H17</i>	1.0832	1.0802
<i>S1C3</i>	1.8376	1.8376 (1.8319)
<i>C3C4</i>	1.4898	1.4871
<i>C4C5</i>	1.3340	1.3322
<i>C3H7</i>	1.0948	1.0918
<i>C3H6</i>	1.0891	1.0861
<i>C4H8</i>	1.0862	1.0832
<i>C5H10</i>	1.0829	1.0799
<i>C5H11</i>	1.0844	1.0814
<i>C11S2S1</i>	102.71	
<i>C12C11S2</i>	112.98	
<i>C13C12C11</i>	123.57	
<i>H14C11S2</i>	108.50	
<i>H15C11S2</i>	103.21	
<i>H16C12C11</i>	116.37	
<i>H18C13C12</i>	121.13	
<i>H17C13C12</i>	121.41	
<i>C3S1S2</i>	103.57	
<i>C4C3S1</i>	112.14	
<i>C5C4C3</i>	123.45	
<i>H7C3S1</i>	102.98	
<i>H6C3S1</i>	108.72	
<i>H8C4C3</i>	116.47	
<i>H10C5C4</i>	121.44	
<i>H9C5C4</i>	121.13	
<i>C12C11S2S1</i>	67.83	
<i>C13C12C3</i>	-113.62	
<i>H14C11S2S1</i>	-56.49	
<i>H15C11S2S1</i>	-171.66	
<i>H16C12C3S2</i>	64.79	
<i>H18C13C12C11</i>	-0.84	
<i>H17C13C12C11</i>	179.24	
<i>C3S1S2C11</i>	-93.12	
<i>C4C3S1S2</i>	-64.52	
<i>C5C4C3S1</i>	113.08	
<i>H7C3S1S2</i>	175.35	
<i>H6C3S1S2</i>	60.04	
<i>H8C4C3S1</i>	-64.60	
<i>H10C5C4C3</i>	-178.67	
<i>H9C5C4C3</i>	1.26	



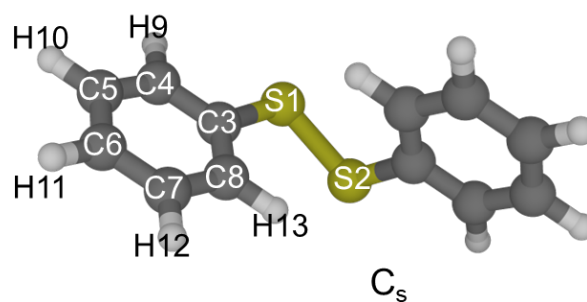
**Table S3.** revDSD and TM(+LR) parameters for diisopropyl disulfide ( $C_3H_7)_2S_2$ , bonds in Å, angles in degrees.

	revDSD	TM (+LR)
S1S2	2.0398	2.0302
C3S1	1.8369	1.8369 (1.8312)
C4C3	1.5208	1.5235
C5C3	1.5264	1.5179 (1.5180)
C3H6	1.0931	1.0899
H10C5	1.0934	1.0902
H12C5	1.0915	1.0883
H11C5	1.0929	1.0897
H8C4	1.0908	1.0876
H7C4	1.0927	1.0895
H9C4	1.0943	1.0911
C3S1S2	103.53	
C5C3S1	106.09	
C4C3S1	111.87	
H6C3S1	106.67	
H10C5C3	110.59	
H12C5C3	111.60	
H11C5C3	109.73	
H8C4C3	111.05	
H7C4C3	110.30	
H9C4C3	110.04	
C5C3S1S2	-172.28	
C4C3S1S2	65.03	
C3S2S1C3b	86.90	
H6C3S1S2	-55.46	
H10C5C3S1	-61.35	
H12C5C3S1	59.40	
H11C5C3S1	179.69	
H8C4C3S1	-57.92	
H7C4C3S1	62.44	
H9C4C3S1	-177.86	



**Table S4.** revDSD and TM(+LR) parameters for diphenyl disulfide ( $C_6H_5)_2S_2$ , bonds Å, in angles in degrees.

	revDSD	TM+LR
<i>S1S2</i>	2.0279	2.0183
<i>C3S1</i>	1.7828	1.7828 (1.7777)
<i>C3C4</i>	1.3989	1.3966
<i>C4C5</i>	1.3911	1.3888
<i>C5C6</i>	1.3945	1.3922
<i>C6C7</i>	1.3926	1.3903
<i>C7C8</i>	1.3941	1.3918
<i>C4H9</i>	1.0847	1.0809
<i>C5H10</i>	1.0836	1.0798
<i>C6H11</i>	1.0831	1.0793
<i>C7H12</i>	1.0837	1.0799
<i>C8H13</i>	1.0827	1.0789
<i>C3S1S2</i>	105.52	
<i>C4C3S1</i>	115.61	
<i>C5C4C3</i>	119.82	
<i>C6C5C4</i>	120.29	
<i>C7C6C5</i>	119.55	
<i>C8C7C6</i>	120.66	
<i>H9C4C3</i>	119.99	
<i>H10C5C4</i>	119.50	
<i>H11C6C5</i>	120.21	
<i>H12C7C6</i>	120.09	
<i>H13C8C7</i>	120.34	
<i>C4C3S1S2</i>	-168.32	
<i>C5C4C3S1</i>	-178.21	
<i>C6C5C4C3</i>	-0.24	
<i>C7C6C5C4</i>	0.11	
<i>C8C7C6C5</i>	0.23	
<i>H9C4C3S1</i>	2.17	
<i>H10C5C4C3</i>	-179.79	
<i>H11C6C5C4</i>	-179.77	
<i>H12C7C6C5</i>	179.97	
<i>H13C8C7C6</i>	-179.90	
<i>C3S1S2C3b</i>	-84.63	



**Table S5.** RSSR disulfide linkage structural parameters computed by DFT for H<sub>2</sub>S<sub>2</sub>, bonds in Å, angles in degrees.

H <sub>2</sub> S <sub>2</sub>	SS	SH	HSS	HSSH
<b>BestEst</b>	2.0503	1.3395	98.18	90.64
revDSD	2.0609	1.3422	98.24	90.63
B3LYP	2.0758	1.3475	98.57	90.71
B3LYPD3BJ	2.0752	1.3473	98.49	90.64
B3PW91	2.0562	1.3475	98.62	90.76
B3PW91-D3BJ	2.0554	1.3476	98.57	90.64
CAM-B3LYP	2.0590	1.3422	98.54	90.71
CAM-B3LYP-D3BJ	2.0581	1.3423	98.51	90.67
PBE0	2.0481	1.3469	98.64	90.71
PBE0-D3BJ	2.0485	1.3470	98.55	90.67
LC-wPBE	2.0324	1.3394	98.51	90.74
LC-wPBE-D3BJ	2.0323	1.3393	98.49	90.70
B97	2.0786	1.3476	98.39	90.76
B97D3BJ	2.0735	1.3519	98.59	90.63
wB97X	2.0428	1.3402	98.51	90.77
wB97XD3-BJ	2.0397	1.3399	98.45	90.73
APF	2.0512	1.3473	98.63	90.71
APFD	2.0524	1.3477	98.80	90.50
M062X	2.0553	1.3405	98.22	90.81
M062XD3	2.0553	1.3405	98.22	90.82
MN15	2.0400	1.3354	98.66	90.80
B2PLYP	2.0664	1.3419	98.41	90.67
B2PLYPD3BJ	2.0661	1.3418	98.38	90.65
DSDPBEP86	2.0585	1.3417	98.25	90.61
DSDPBEP86h95	2.0498	1.3384	98.26	90.64
DSDPBEP86h95_D3BJ	2.0530	1.3395	98.23	90.61
PBE0DH	2.0399	1.3396	98.56	90.68
PBEQIDH	2.0391	1.3366	98.46	90.64

**Table S6.** RSSR disulfide linkage structural parameters computed by DFT for dimethyl disulfide (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub>, bonds in Å, angles in degrees.

(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>	SS	SC	SSC	CSSC
<b>Grad-MP2-CCSD(T)</b>	2.0298	1.8077	102.35	84.77
<b>revDSD</b>	2.0409	1.8149	102.49	85.21
<b>B3LYP</b>	2.0521	1.8247	104.05	87.10
<b>B3LYPD3BJ</b>	2.0498	1.8226	103.29	85.20
<b>B3PW91</b>	2.0344	1.8123	104.13	87.27
<b>B3PW91-D3BJ</b>	2.0359	1.8095	103.17	85.04
<b>CAM-B3LYP</b>	2.0363	1.8088	103.50	86.28
<b>CAM-B3LYP-D3BJ</b>	2.0387	1.8071	103.04	85.06
<b>PBE0</b>	2.0304	1.8049	103.57	86.18
<b>PBE0-D3BJ</b>	2.0297	1.8041	103.22	85.10
<b>LC-wPBE</b>	2.0168	1.7919	103.01	85.80
<b>LC-wPBE-D3BJ</b>	2.0162	1.7914	102.68	84.68
<b>B97</b>	2.0604	1.8272	103.63	86.89
<b>B97D3BJ</b>	2.0459	1.8281	103.60	85.20
<b>wB97X</b>	2.0261	1.8016	102.93	85.28
<b>wB97XD3-BJ</b>	2.0207	1.7981	102.03	83.22
<b>APF</b>	2.0334	1.8074	103.71	86.57
<b>APFD</b>	2.0351	1.8100	103.68	84.64
<b>M062X</b>	2.0347	1.8104	102.40	84.91
<b>M062XD3</b>	2.0348	1.8104	102.41	84.98
<b>MN15</b>	2.0169	1.7964	102.09	83.56
<b>B2PLYP</b>	2.0437	1.8181	103.32	86.20
<b>B2PLYPD3BJ</b>	2.0428	1.8172	102.99	85.29
<b>DSDPBEP86</b>	2.0369	1.8120	102.50	85.03
<b>DSDPBEB95</b>	2.0317	1.8061	102.43	84.98
<b>DSDPBEB95_D3BJ</b>	2.0345	1.8082	102.24	84.57
<b>PBE0DH</b>	2.0196	1.7982	103.34	85.95
<b>PBEQIDH</b>	2.0192	1.7974	102.95	85.52

**Table S7.** RSSR disulfide linkage structural parameters computed by DFT for diethyl disulfide (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>S<sub>2</sub>, bonds in Å, angles in degrees.

(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>2</sub>	SS	SC	SSC	CSSC
<b>TM+LR</b>	2.0333	1.8187	102.76	87.24
<b>revDSD</b>	2.0429	1.8243	102.76	87.24
<b>B3LYP</b>	2.0551	1.8376	104.44	89.17
<b>B3LYPD3BJ</b>	2.0514	1.8341	103.58	86.60
<b>B3PW91</b>	2.0367	1.8249	104.43	88.95
<b>B3PW91-D3BJ</b>	2.0361	1.8217	103.42	84.96
<b>CAM-B3LYP</b>	2.0391	1.8196	103.86	88.54
<b>CAM-B3LYP-D3BJ</b>	2.0403	1.8182	103.37	86.23
<b>PBE0</b>	2.0322	1.8175	103.84	87.78
<b>PBE0-D3BJ</b>	2.0309	1.8163	103.47	85.78
<b>LC-wPBE</b>	2.0181	1.8018	103.30	87.54
<b>LC-wPBE-D3BJ</b>	2.0168	1.8006	102.95	85.43
<b>B97</b>	2.0634	1.8398	103.95	88.35
<b>B97D3BJ</b>	2.0471	1.8410	103.90	86.39
<b>wB97X</b>	2.0276	1.8119	103.36	87.21
<b>wB97XD3-BJ</b>	2.0215	1.8069	102.40	84.81
<b>APF</b>	2.0351	1.8203	104.01	88.11
<b>APFD</b>	2.0359	1.8240	103.90	84.39
<b>M062X</b>	2.0368	1.8210	102.67	87.29
<b>M062XD3</b>	2.0369	1.8210	102.68	87.21
<b>MN15</b>	2.0194	1.8064	102.22	86.18
<b>B2PLYP</b>	2.0464	1.8296	103.67	88.42
<b>B2PLYPD3BJ</b>	2.0448	1.8281	103.28	87.16
<b>DSDPBEP86</b>	2.0390	1.8219	102.78	87.18
<b>DSDPBEhB95</b>	2.0359	1.8173	102.57	85.99
<b>DSDPBEhB95_D3BJ</b>	2.0347	1.8162	102.32	85.11
<b>PBE0DH</b>	2.0217	1.8090	103.61	87.93
<b>PBEQIDH</b>	2.0212	1.8076	103.21	87.60

**Table S8.** RSSR disulfide linkage structural parameters computed by DFT for diallyl disulfide (C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>S<sub>2</sub>, bonds in Å, angles in degrees.

(C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>2</sub>	SS	S2C3	S1C11	SSC3	SSC11	CSSC
<b>TM+LR</b>	2.0268	1.8294	1.8319	103.57	103.57	-93.12
<b>revDSD</b>	2.0364	1.8351	1.8376	103.57	103.57	-93.12
<b>B3LYP</b>	2.0509	1.8518	1.8543	104.41	105.33	-93.89
<b>B3LYPD3BJ</b>	2.0449	1.8475	1.8524	103.37	104.18	-91.01
<b>B3PW91</b>	2.0332	1.8377	1.8397	104.28	105.14	-94.22
<b>B3PW91-D3BJ</b>	2.0283	1.8352	1.8393	103.26	103.97	-92.02
<b>CAM-B3LYP</b>	2.0369	1.8291	1.8309	103.80	104.76	-93.37
<b>CAM-B3LYP-D3BJ</b>	2.0351	1.8278	1.8309	103.44	104.39	-91.73
<b>PBE0</b>	2.0255	1.8286	1.8312	103.84	104.72	-93.00
<b>PBE0-D3BJ</b>	2.0234	1.8273	1.8313	103.43	104.26	-91.46
<b>LC-wPBE</b>	2.0139	1.8074	1.8087	103.26	104.17	-93.28
<b>LC-wPBE-D3BJ</b>	2.0119	1.8062	1.8086	102.86	103.76	-91.67
<b>B97</b>	2.0553	1.8534	1.8565	104.01	104.89	-93.19
<b>B97D3BJ</b>	2.0385	1.8604	1.8667	103.81	104.42	-91.57
<b>wB97X</b>	2.0225	1.8185	1.8213	103.41	104.35	-91.75
<b>wB97XD3-BJ</b>	2.0155	1.8138	1.8176	102.53	103.45	-90.95
<b>APF</b>	2.0282	1.8319	1.8343	103.97	104.86	-93.33
<b>APFD</b>	2.0275	1.8331	1.8382	103.76	104.52	-90.26
<b>M062X</b>	2.0329	1.8320	1.8343	102.54	103.29	-93.16
<b>M062XD3</b>	2.0330	1.8319	1.8342	102.56	103.32	-93.17
<b>MN15</b>	2.0181	1.8180	1.8220	102.59	103.30	-93.26
<b>B2PLYP</b>	2.0384	1.8233	1.8246	104.22	105.30	-94.11
<b>B2PLYPD3BJ</b>	2.0382	1.8401	1.8440	103.05	103.86	-91.92
<b>DSDPBEP86</b>	2.0327	1.8317	1.8348	102.53	103.32	-92.37
<b>DSDPBEh95</b>	2.0296	1.8284	1.8307	102.65	103.35	-93.11
<b>DSDPBEhB95_D3BJ</b>	2.0279	1.8272	1.8305	102.42	103.10	-92.50
<b>PBE0DH</b>	2.0188	1.8192	1.8213	103.38	104.25	-93.26
<b>PBEQIDH</b>	2.0177	1.8181	1.8203	102.93	103.72	-93.19

**Table S9.** RSSR disulfide linkage structural parameters computed by DFT for diisopropyl disulfide (C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>S<sub>2</sub>, bonds in Å, angles in degrees.

(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> S <sub>2</sub>	SS	SC	SSC	CSSC
<b>TM+LR</b>	2.0302	1.8312	103.53	86.90
revDSD	2.0398	1.8369	103.53	86.90
B3LYP	2.0524	1.8575	104.93	88.60
B3LYPD3BJ	2.0484	1.8515	104.02	85.45
B3PW91	2.0347	1.8432	104.94	88.45
B3PW91-D3BJ	2.0310	1.8378	104.06	84.78
CAM-B3LYP	2.0373	1.8360	104.35	88.31
CAM-B3LYP-D3BJ	2.0355	1.8340	103.94	86.28
PBE0	2.0279	1.8346	104.62	87.95
PBE0-D3BJ	2.0260	1.8324	104.18	85.73
LC-wPBE	2.0146	1.8152	103.97	88.08
LC-wPBE-D3BJ	2.0128	1.8131	103.51	85.76
B97	2.0587	1.8589	104.65	88.22
B97D3BJ	2.0434	1.8606	104.41	85.30
wB97X	2.0236	1.8267	104.08	87.65
wB97XD3-BJ	2.0175	1.8184	103.15	85.16
APF	2.0308	1.8379	104.75	88.24
APFD	2.0305	1.8379	104.50	84.58
M062X	2.0346	1.8335	103.42	87.28
M062XD3	2.0346	1.8335	103.39	87.07
MN15	2.0217	1.8213	102.96	85.88
B2PLYP	2.0437	1.8451	104.19	87.43
B2PLYPD3BJ	2.0419	1.8425	103.74	85.82
DSDPBEP86	2.0362	1.8333	103.25	85.74
DSDPBEB95	2.0327	1.8310	103.30	86.32
DSDPBEB95_D3BJ	2.0314	1.8291	103.03	85.40
PBE0DH	2.0200	1.8230	104.16	87.40
PBEQIDH	2.0191	1.8198	103.74	86.65

**Table S10.** RSSR disulfide linkage structural parameters computed by DFT for diphenyl disulfide (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>S<sub>2</sub>, bonds Å, in angles in degrees.

(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S <sub>2</sub>	SS	SC	CSS	CSSC
<b>TM+LR</b>	2.0183	1.7777	105.52	-84.63
<b>revDSD</b>	2.0279	1.7828	105.52	-84.63
<b>B3LYP</b>	2.0398	1.7934	107.09	-89.82
<b>B3LYPD3BJ</b>	2.0367	1.7876	106.12	-85.27
<b>B3PW91</b>	2.0364	1.7876	106.59	-89.55
<b>B3PW91-D3BJ</b>	2.0334	1.7823	105.59	-83.69
<b>CAM-B3LYP</b>	2.0358	1.7850	105.95	-85.93
<b>CAM-B3LYP-D3BJ</b>	2.0358	1.7850	105.95	-85.93
<b>PBE0</b>	2.0292	1.7819	106.31	-88.64
<b>PBE0-D3BJ</b>	2.0277	1.7795	105.81	-85.35
<b>LC-wPBE</b>	2.0134	1.7744	106.04	-88.00
<b>LC-wPBE-D3BJ</b>	2.0116	1.7722	105.54	-84.20
<b>B97</b>	2.0589	1.8012	106.47	-90.02
<b>B97D3BJ</b>	2.0506	1.7960	106.03	-84.84
<b>wB97X</b>	2.0246	1.7832	106.10	-87.71
<b>wB97XD3-BJ</b>	2.0180	1.7764	105.22	-83.33
<b>APF</b>	2.0320	1.7842	106.43	-89.01
<b>APFD</b>	2.0340	1.7848	106.09	-84.12
<b>M062X</b>	2.0231	1.7802	105.70	-85.57
<b>M062XD3</b>	2.0230	1.7803	105.70	-85.18
<b>MN15</b>	2.0056	1.7660	105.74	-86.81
<b>B2PLYP</b>	2.0316	1.7868	106.31	-87.54
<b>B2PLYPD3BJ</b>	2.0299	1.7843	105.87	-84.93
<b>DSDPBEP86</b>	2.0240	1.7801	105.47	-84.56
<b>DSDPBEh95</b>	2.0301	1.7799	105.29	-84.85
<b>DSDPBEh95_D3BJ</b>	2.0321	1.7811	105.14	-83.75
<b>PBE0DH</b>	2.0072	1.7697	106.17	-87.20
<b>PBEQIDH</b>	2.0066	1.7683	105.78	-85.74