Supporting Information

The Challenging Equilibrium Structure of HSSH: Another Success of the Rotational Spectroscopy / Quantum Chemistry Synergism

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Table S1. Calculation with the valence and all electron correlation at CCSD(T) level.

CVTZ	All electrons correlated	Frozen core	Δ [a]
SS(Å)	2.0678	2.0716	0.0038
SH(Å)	1.3402	1.3419	0.0017
HSS (deg)	97.94	97.95	0.00
HSSH (deg)	90.49	90.48	0.01
wCVTZ	All electrons correlated	Frozen core	Δ [b]
SS(Å)	2.0643	2.0689	0.0046
SH(Å)	1.3384	1.3402	0.0018
HSS (deg)	97.99	97.99	0.01
HSSH (deg)	90.50	90.49	0.01

[a] Δ = CCSD(T)/CVTZ/all electrons correlated – CCSD(T)/CVTZ/frozen core;

[b] Δ = CCSD(T)/wCVTZ/all electrons correlated – CCSD(T)/wCVTZ/frozen core.

Table S2. B_0^{exp}, ΔB_{vib} and ΔB_{el} for HSSH. All data are in MHz.

		B_0^{exp}	ΔB_{vib}(cc-pVTZ)					ΔB_{el}
			B2PLYP	B2PLYP-D3BJ	B3LYP	B3LYP-D3BJ	MP2	MP2/cc-pVTZ
HSSH	A	146858.1658(11)	-1091.686	-1092.350	-1119.338	-1122.338	-1028.188	21.890
	B	6970.42679(15)	-46.367	-46.280	-45.322	-45.148	-46.151	-0.105
	C	6967.68576(14)	-47.274	-47.191	-46.082	-45.934	-47.396	-0.104
$HS^{34}SH$	A	146694.9773(20)	-1029.589	-1046.522	-1053.295	-1089.823	-983.574	21.853
	B	6779.01770(15)	-45.207	-45.019	-44.762	-44.289	-44.759	-0.099
	C	6776.33850(27)	-46.059	-45.851	-45.570	-45.028	-45.807	-0.098
HSSD	A	100567.3952(14)	-562.283	-563.386	-570.070	-572.153	-537.837	10.131
	B	6826.36107(16)	-39.744	-39.662	-39.423	-39.262	-39.025	-0.100
	C	6677.79089(16)	-43.706	-43.629	-43.369	-43.215	-43.075	-0.096
DSSD	A	76459.8310(10)	-684.908	-682.783	-729.935	-724.123	-591.000	5.788
	B	6542.74398(14)	-37.082	-37.014	-36.826	-36.685	-36.634	-0.091
	C	6542.72004(14)	-29.286	-29.262	-29.015	-28.979	-28.843	-0.093
			ΔB_{vib}(aug-cc-pVTZ)					ΔB_{el}
HSSH	A	146858.1658(11)	-1088.799	-1089.496	-1113.043	-1114.456	-1031.820	21.890
	B	6970.42679(15)	-46.420	-46.332	-45.283	-45.032	-46.268	-0.105
	C	6967.68576(14)	-47.234	-47.148	-45.876	-45.685	-47.553	-0.104
$HS^{34}SH$	A	146694.9773(20)	-1052.964	-1052.248	-1090.960	-1087.325	-984.823	21.853
	B	6779.01770(15)	-45.122	-45.063	-44.322	-44.245	-44.863	-0.099
	C	6776.33850(27)	-46.037	-45.974	-45.126	-45.063	-45.962	-0.098
HSSD	A	100567.3952(14)	-559.975	-561.033	-566.413	-568.439	-538.646	10.131
	B	6826.36107(16)	-39.745	-39.662	-39.248	-39.078	-39.175	-0.100
	C	6677.79089(16)	-43.738	-43.660	-43.226	-43.068	-43.264	-0.096
DSSD	A	76459.8310(10)	-686.032	-683.883	-728.151	-722.288	-596.908	5.788
	B	6542.74398(14)	-29.353	-36.976	-28.941	-36.436	-29.033	-0.091

	C	6542.72004(14)	-37.043	-29.330	-36.580	-28.906	-36.864	-0.093

Table S3. MAE and |MAX| of semi-experimental equilibrium structure of HSSH compare with "best estimate" structure.

VTZ										
	r_e^{SE}					r_e				
	B2PLYP	B2PLYP-D3BJ	B3LYP	B3LYP-D3BJ	MP2	B2PLYP	B2PLYP-D3BJ	B3LYP	B3LYP-D3BJ	MP2
MAE [a]	0.0010	0.0009	0.0009	0.0009	0.0011	0.0156	0.0155	0.0229	0.0225	0.0076
|MAX| [a]	0.0010	0.0010	0.0012	0.0013	0.0013	0.0264	0.0261	0.0356	0.0350	0.0151
MAE [b]	0.08	0.08	0.12	0.14	0.03	0.05	0.08	0.09	0.09	0.19
|MAX| [b]	0.10	0.11	0.16	0.19	0.04	0.08	0.11	0.16	0.10	0.38
AVTZ										
	r_e^{SE}					r_e				
	B2PLYP	B2PLYP-D3BJ	B3LYP	B3LYP-D3BJ	MP2	B2PLYP	B2PLYP-D3BJ	B3LYP	B3LYP-D3BJ	MP2
MAE [a]	0.0009	0.0009	0.0008	0.0009	0.0010	0.0163	0.0161	0.0231	0.0227	0.0086
|MAX| [a]	0.0011	0.0010	0.0014	0.0013	0.0011	0.0276	0.0273	0.0364	0.0358	0.0164
MAE [b]	0.10	0.07	0.12	0.12	0.08	0.09	0.09	0.19	0.11	0.36
|MAX| [b]	0.11	0.08	0.16	0.12	0.09	0.16	0.14	0.19	0.12	0.42

[a] Mean absolute error (MAE) and maximum absolute deviations (|MAX|) with respect to the structure from "best estimate" method for bond lengths. [b] Mean absolute error (MAE) and maximum absolute deviations (|MAX|) with respect to the structure from "best estimate" method for angles.

Table S4. XYZ coordinates of structures from theoretical and semi-experimental schemes.

	best estimate		
	X	Y	Z
S	0.00000	0.00000	0.00000
S	0.00000	0.00000	2.05030
H	1.32587	0.00000	2.24089
H	-0.01481	-1.32579	-0.19059
	SE-B2PLYPD3BJ-AVTZ		
	X	Y	Z
S	0.00000	0.00000	0.00000
S	0.00000	0.00000	2.05130
H	1.32683	0.00000	2.24084
H	-0.01667	-1.32672	-0.18954

Results with other methods .xyz files, can be found in zipped attachment.