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On the possible biological relevance of HSNO isomers: A computational investigation

Supplementary Information

Supplementary Tables, Figures Cartesian Coordinates and Energies

Lena V. Ivanova, Becka J. Anton and Qadir K. Timerghazin*

Department of Chemistry, Marquette University, .PO. Box 1881, Milwaukee, Wisconsin 53201-1881

E-mail: qadir.timerghazin@marquette.edu

* To whom correspondence should be addressed

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Supplementary Tables S1-S8

Table S1 Calculated bond lengths, angles and dihedral angles for HSNO isomers and transition states TS1-TS6, see Figure 2

trans-HSNO	r(S–N)/Å	r(N–O)/Å	∠S–N–O/°	r(S-H)/Å	∠N–S-H/°	∠S–N-H-O/°	E, Hartree
CCSD(T)/							
AVDZ	1.903	1.189	114.50	1.350	89.66	180.00	-527.912777
AVTZ	1.860	1.183	114.55	1.339	90.18	180.00	-528.066835
AVQZ	1.846	1.181	114.54	1.338	90.46	180.00	-528.114060
AV5Z	1.841	1.181	114.50	1.338	90.54	180.00	-528.129071
AV5Z//AVQZ							-528.129067
CBS	1.837	1.181	114.47	1.338	90.61	180.00	-528.141302
CBS_{TQ}	1.836	1.180	114.53	1.337	90.66	180.00	-528.148521
CBS_{Q5sp}							-528.144813
ΔQ	0.033	-0.001	0.34	0.001	-0.69	0.00	-0.004970
ΔCV	-0.007	-0.001	0.01	-0.002	0.06	0.00	-0.433051
ΔSR	-0.005	0.001	-0.07	0.003	-0.07	0.00	-1.462397
CBS+CORR	1.858	1.180	114.74	1.340	89.90	180.00	
CBS_{TQ}+CORR	1.856	1.179	114.81	1.339	89.96	180.00	
PBE0/def2-TZVPPD	1.828	1.167	115.31	1.340	90.68	180.00	-528.473530
CBS-QB3	1.929	1.163	115.27	1.342	89.59	180.00	-528.099521

cis-HSNO	r(S–N)/Å	r(N–O)/Å	∠S-N-O/°	r(S–H)/Å	∠N-S-H/°	∠S-N-H-O/°	E, Hartree
CCSD(T)/							
AVDZ	1.894	1.192	115.49	1.356	94.28	0.00	-527.911100
AVTZ	1.847	1.187	115.76	1.345	94.88	0.00	-528.065296
AVQZ	1.830	1.184	115.88	1.345	95.28	0.00	-528.112573
AV5Z	1.825	1.184	115.87	1.345	95.35	0.00	-528.127616
AV5Z//AVQZ							-528.127611
CBS	1.821	1.184	115.86	1.345	95.41	0.00	-528.139872
CBS_{TQ}	1.818	1.182	115.97	1.345	95.57	0.00	-528.147073
CBS_{Q5sp}							-528.143389
ΔQ	0.034	-0.001	0.04	0.000	-0.41	0.00	-0.004807
ΔCV	-0.008	-0.001	0.07	-0.002	0.08	0.00	-0.433065
ΔSR	-0.005	0.001	-0.04	0.002	-0.15	0.00	-1.462393
CBS+CORR	1.842	1.183	115.93	1.345	94.92	0.00	
CBS_{TQ}+CORR	1.839	1.181	116.04	1.345	95.09	0.00	

PBE0/def2-TZVPPD	1.811	1.170	116.95	1.348	96.89	0.00	-528.471823
CBS-QB3	1.917	1.165	116.24	1.348	95.75	0.00	-528.097713

cis-HONS	r(S–N)/Å	r(N–O)/Å	∠S–N–O/°	r(O–H)/Å	∠N-O-H/°	∠H-O-N-S/°	E, Hartree
CCSD(T)/							
AVDZ	1.608	1.374	115.85	0.986	107.02	0.00	-527.903999
AVTZ	1.591	1.361	115.99	0.982	106.72	0.00	-528.061071
AVQZ	1.585	1.355	116.11	0.979	106.87	0.00	-528.108907
AV5Z	1.582	1.353	116.12	0.979	106.88	0.00	-528.124176
AV5Z//AVQZ							-528.124170
CBS	1.580	1.352	116.13	0.978	106.89	0.00	-528.136615
CBS_{TQ}	1.580	1.350	116.19	0.977	106.98	0.00	-528.143814
CBS_{Q5sp}							-528.140183
ΔQ	0.003	0.003	-0.12	0.001	-0.08	0.00	-0.003484
ΔCV	-0.004	-0.003	0.07	-0.001	0.05	0.00	-0.433243
ΔSR	0.001	0.000	-0.01	0.000	-0.16	0.00	-1.462856
CBS+CORR	1.581	1.353	116.06	0.979	106.70	0.00	
CBS_{TQ}+CORR	1.581	1.350	116.13	0.978	106.79	0.00	
PBE0/def2-TZVPPD	1.571	1.325	117.16	0.981	107.96	0.00	-528.465012
CBS-QB3	1.585	1.340	116.87	0.985	108.16	0.00	-528.094847

trans-HONS	r(S–N)/Å	r(N–O)/Å	∠S–N–O/°	r(O–H)/Å	∠N-O-H/°	∠H-O-N-S/°	E, Hartree
CCSD(T)/							
AVDZ	1.597	1.403	112.42	0.974	102.18	180.00	-527.903926
AVTZ	1.581	1.389	112.85	0.969	102.30	180.00	-528.060857
AVQZ	1.575	1.382	113.04	0.967	102.49	180.00	-528.108505
AV5Z	1.573	1.380	113.10	0.966	102.48	180.00	-528.123730
AV5Z//AVQZ							-528.123724
CBS	1.571	1.379	113.15	0.966	102.48	180.00	-528.136134
CBS_{TQ}	1.571	1.376	113.18	0.965	102.64	180.00	-528.143275
CBS_{Q5sp}							-528.139692
ΔQ	0.003	0.005	-0.12	0.001	-0.15	0.00	-0.003546
ΔCV	-0.004	-0.003	0.69	-0.001	0.09	0.00	-0.433269
ΔSR	0.001	0.001	-0.08	0.000	-0.03	0.00	-1.462861

CBS+Q+CV+SR	1.571	1.382	113.63	0.966	102.39	180.00	
CBS_{TQ}+Q+CV+SR	1.571	1.378	113.66	0.965	102.55	180.00	
PBE0/def2-TZVPPD	1.562	1.352	114.30	0.966	103.55	180.00	-528.463676
CBS-QB3	1.573	1.378	113.92	0.969	103.81	180.00	-528.094829

SN(H)O	r(S–N)/Å	r(N–O)/Å	r(S–O)/Å	r(N–H)/Å	∠ S-N-O/°	∠S-O-N-H/°	E, Hartree
CCSD(T)/							
AVDZ	1.647	1.248	2.619	1.036	129.07	180.00	-527.905638
AVTZ	1.629	1.239	2.597	1.028	129.20	180.00	-528.063319
AVQZ	1.624	1.236	2.588	1.027	129.17	180.00	-528.111178
AV5Z	1.622	1.235	2.585	1.027	129.16	180.00	-528.126249
AV5Z//AVQZ							-528.126244
CBS	1.620	1.234	2.58	1.027	129.16	180.00	-528.138527
CBS_{TQ}	1.620	1.233	2.582	1.027	129.14	180.00	-528.146102
CBS_{Q5sp}							-528.142052
ΔQ	0.006	0.003	0.006	0.000	-0.14	0.00	-0.004226
ΔCV	-0.003	-0.002	-0.005	-0.001	0.00	0.00	-0.433514
ΔSR	0.001	0.000	0.001	0.000	0.01	0.00	-1.462709
CBS+CORR	1.624	1.235	2.586	1.026	129.03	180.00	
CBS_{TQ}+CORR	1.624	1.233	2.585	1.026	129.02	180.00	
CASPT2/							
AVDZ	1.629	1.266	2.606	1.030	127.97	180.79	-527.867613
AVTZ	1.616	1.256	2.588	1.023	128.16	180.59	-528.019999
AVQZ	1.611	1.253	2.580	1.022	128.15	180.58	-528.071418
AV5Z	1.609	1.251	2.578	1.022	128.16	180.59	-528.090422
CBS	1.608	1.251	2.576	1.022	128.17	180.59	-528.105922
PBE0/def2-TZVPPD	1.616	1.216	2.569	1.031	129.75	180.00	-528.471460
CBS-QB3	1.636	1.223	2.594	1.035	129.65	180.00	-528.098559

cycl-SONH	r(S–N)/Å	r(N–O)/Å	r(S–O)/Å	r(N–H)/Å	∠ S-N-O/°	∠S-O-N-H/°	E, Hartree
CCSD(T)/							
AVDZ	1.789	1.484	1.744	1.039	63.61	99.51	-527.858999
AVTZ	1.754	1.473	1.702	1.028	62.97	99.88	-528.021590
AVQZ	1.745	1.468	1.694	1.026	62.94	100.01	-528.069302
AV5Z	1.743	1.466	1.691	1.026	62.90	100.04	-528.084775

AV5Z//AVQZ							-528.084767
CBS	1.740	1.465	1.688	1.026	62.87	100.07	-528.097383
CBS_{TQ}	1.739	1.463	1.688	1.025	62.91	100.11	-528.104119
CBS_{Q5sp}							-528.100992
ΔQ	0.003	0.003	0.004	0.001	0.04	-0.02	-0.003041
ΔCV	-0.003	-0.003	-0.004	-0.001	-0.04	0.02	-0.433020
ΔSR	0.002	0.000	0.002	0.000	0.02	-0.10	-1.462624
CBS+CORR	1.742	1.465	1.690	1.026	62.88	99.97	
CBS_{TQ}+CORR	1.741	1.464	1.689	1.025	62.93	100.01	
CASPT2/							
AVDZ	1.795	1.480	1.749	1.035	63.70	99.17	-527.815728
AVTZ	1.761	1.470	1.707	1.026	63.02	99.46	-527.973084
AVQZ	1.753	1.464	1.699	1.024	63.00	99.60	-528.024190
AV5Z	1.750	1.463	1.696	1.023	62.97	99.62	-528.043495
CBS	1.748	1.462	1.693	1.023	62.94	99.64	-528.059243
PBE0/def2-TZVPPD	1.728	1.438	1.678	1.026	63.25	100.4	-528.425327
CBS-QB3	1.769	1.448	1.731	1.029	64.19	99.8	-528.054377

TS1	r(S–N)/Å	r(N–O)/Å	∠S-N-O/°	r(S–H)/Å	∠N-S-H/°	∠O-N-S-H/°	E, Hartree
CCSD(T)/							
AVDZ	2.067	1.171	112.92	1.353	87.17	87.63	-527.899905
AVTZ	2.031	1.161	112.99	1.342	87.40	87.48	-528.053098
AVQZ	2.019	1.158	113.00	1.341	87.65	87.51	-528.099954
AV5Z	2.015	1.157	112.95	1.341	87.69	87.51	-528.114847
AV5Z//AVQZ							-528.114843
CBS	2.012	1.157	112.91	1.341	87.72	87.51	-528.126980
CBS_{TQ}	2.010	1.156	113.01	1.341	87.83	87.53	-528.134146
CBS_{Q5sp}							-528.130465
ΔQ	0.025	0.000	0.03	0.001	-0.31	0.45	-0.004115
ΔCV	-0.007	-0.001	0.02	-0.002	0.05	-0.02	-0.432882
ΔSR	0.006	-0.001	-0.03	0.003	-0.20	0.08	-1.462547
CBS+CORR	2.035	1.155	112.94	1.342	87.26	88.02	
CBS_{TQ}+CORR	2.034	1.154	113.04	1.342	87.36	88.05	
	1.983	1.144	113.59	1.343	88.45	87.89	-528.455912

CBS-QB3	2.082	1.145	113.35	1.346	87.97	87.87	-528.085713

TS2	r(S–N)/Å	r(N–O)/Å	∠S-N-O/°	r(O–H)/Å	∠N-O-H/°	∠S-O-N-H/°	E, Hartree
CCSD(T)/							
AVDZ	1.670	1.288	106.30	1.369	85.26	0.00	-527.860653
AVTZ	1.652	1.276	106.57	1.369	84.89	0.00	-528.017155
AVQZ	1.645	1.272	106.73	1.369	85.00	0.00	-528.064886
AV5Z//AVQZ							-528.080162
CBS_{TQ}	1.639	1.268	106.85	1.368	85.08	0.00	-528.099717
CBS_{Q5sp}							-528.096189
ΔQ	0.005	0.003	-0.08	0.002	0.07	0.00	-0.004316
ΔCV	-0.004	-0.002	0.09	-0.001	-0.01	0.00	-0.433186
ΔSR	0.001	0.000	-0.01	0.001	0.03	0.00	-1.462602
CBS_{TQ}+CORR	1.642	1.268	106.85	1.370	85.18	0.00	
PBE0/def2-TZVPPD	1.633	1.252	107.20	1.364	85.49	0.00	-528.424125
CBS-QB3	1.650	1.259	107.08	1.379	86.05	0.00	-528.049761

TS3	r(S–N)/Å	r(N–O)/Å	∠S-N-O/°	r(O–H)/Å	∠N-O-H/°	∠S-N-O-H/°	E, Hartree
CCSD(T)/							
AVDZ	1.591	1.468	112.78	0.974	103.54	86.77	-527.884963
AVTZ	1.574	1.450	113.13	0.969	103.85	87.00	-528.041580
AVQZ	1.568	1.441	113.31	0.966	104.10	87.15	-528.088894
AV5Z//AVQZ							-528.104088
CBS_{TQ}	1.564	1.435	113.43	0.964	104.29	87.27	-528.123421
CBS_{Q5sp}							-528.120029
ΔQ	0.003	0.003	-0.03	0.001	-0.10	0.15	-0.003220
ΔCV	-0.003	-0.003	0.07	-0.001	0.11	-0.01	-0.433184
ΔSR	0.001	0.001	-0.06	0.000	-0.06	-0.03	-1.462912
CBS_{TQ}+CORR	1.565	1.435	113.42	0.964	104.24	87.38	
PBE0/def2-TZVPPD	1.552	1.409	114.50	0.965	105.94	88.31	-528.440691
CBS-QB3	1.563	1.434	114.03	0.969	105.06	87.94	-528.075230

TS4	r(S–N)/Å	r(N–O)/Å	∠S-N-O/°	r(N–H)/Å	∠S-N-H/°	∠S-N-H-O/°	E, Hartree

CCSD(T)/							
AVDZ	1.605	1.374	124.77	1.180	176.19	179.98	-527.822889
AVTZ	1.586	1.364	125.10	1.171	175.97	180.00	-527.981123
AVQZ	1.581	1.358	125.09	1.171	175.92	180.00	-528.028422
AV5Z//AVQZ	1.579	1.356	125.08	1.171	175.91	180.00	-528.043524
CBS_{TQ}	1.577	1.354	125.08	1.171	175.89	180.00	-528.062937
CBS_{Q5sp}							-528.059368
ΔQ	0.004	0.009	-0.25	0.002	0.41	-0.11	-0.005190
ΔCV	-0.004	-0.002	0.03	0.000	-0.03	0.00	-0.433250
ΔSR	0.002	0.000	-0.06	0.000	0.02	-0.03	-1.462809
CBS_{TQ}+CORR	1.579	1.361	124.80	1.172	176.30	179.86	
PBE0/def2-TZVPPD	1.568	1.329	125.95	1.172	174.90	180.00	-528.386500
CBS-QB3	1.583	1.343	125.63	1.173	175.10	179.72	-528.014943

TS5	r(S–N)/Å	r(N–O)/Å	∠S-N-O/°	r(N–H)/Å	∠S-N-H/°	∠S-O-N-H/°	E, Hartree
CCSD(T)/							
AVDZ	1.767	1.350	88.42	1.037	112.67	113.83	-527.822452
AVTZ	1.731	1.343	88.57	1.028	114.31	115.86	-527.979371
AVQZ	1.724	1.336	88.50	1.026	114.77	116.41	-528.026224
AV5Z//AVQZ							-528.045843
CBS_{TQ}	1.718	1.332	88.45	1.025	115.11	116.80	-528.060414
CBS_{Q5sp}							-528.066426
ΔQ	0.014	0.002	-1.85	0.001	-0.13	-0.98	-0.007044
ΔCV	-0.005	-0.001	-0.17	-0.001	0.19	0.14	-0.433049
ΔSR	0.002	0.000	0.02	0.000	-0.24	-0.26	-1.463009
CBS_{TQ}+CORR	1.729	1.333	86.45	1.025	114.93	115.70	
CASPT2/							
AVDZ	1.789	1.331	91.00	1.035	111.17	113.09	-527.776823
AVTZ	1.759	1.318	91.20	1.027	112.36	114.70	-527.928530
AVQZ	1.751	1.313	91.08	1.025	112.82	115.21	-527.978882
AV5Z	1.749	1.311	91.06	1.025	112.93	115.34	-527.997684
CBS	1.746	1.310	91.04	1.025	113.02	115.45	-528.013020
PBE0/def2-TZVPPD	1.729	1.278	90.03	1.030	116.57	119.69	-528.374193
UPBE0/def2-TZVPPD	1.724	1.319	83.83	1.026	115.03	114.51	-528.390152

CBS-QB3	1.775	1.291	89.34	1.034	114.41	116.60	-528.012542

TS6	r(S–N)/Å	r(N–O)/Å	∠S-N-O/°	r(N–H)/Å	∠S-N-H/°	∠S-N-O-H/°	E, Hartree
CCSD(T)/							
AVDZ	1.774	1.221	124.90	1.264	62.78	95.03	-527.826784
AVTZ	1.728	1.214	126.01	1.273	62.94	107.87	-527.983344
AVQZ	1.717	1.211	126.26	1.276	63.08	112.69	-528.030790
AV5Z//AVQZ							-528.045843
CBS_{TQ}	1.708	1.208	126.44	1.278	63.19	116.20	-528.065413
CBS_{Q5sp}							-528.061635
ΔQ	0.042	0.000	-0.43	-0.013	-0.81	-3.42	-0.005621
ΔCV	-0.007	-0.003	0.40	0.002	0.04	4.95	-0.433389
ΔSR	0.004	0.000	-0.26	-0.001	-0.04	-3.81	-1.462641
CBS_{TQ}+CORR	1.747	1.204	126.15	1.267	62.37	113.93	
PBE0/def2-TZVPPD	1.692	1.194	127.58	1.282	62.93	-179.97	-528.393215
CBS-QB3	1.725	1.200	127.56	1.290	62.72	157.43	-528.017478

Table S2 Calculated T_1 and D_1 coupled cluster diagnostics for HSNO isomers and transition states TS1-TS6 at CCSD(T)/AVQZ, see Figure 2

structure	T_1	D_1
cycl-SONH	0.016	0.046
SN(H)O	0.022	0.069
trans-HONS	0.021	0.057
cis-HONS	0.022	0.067
trans-HSNO	0.027	0.079
cis-HSNO	0.026	0.077
TS1	0.022	0.074
TS2	0.029	0.101
TS3	0.019	0.048
TS4	0.029	0.091
TS5	0.073	0.303
TS6	0.030	0.093

Table S3 CASPT2 energy calculations for reaction SN(H)O→cycl-SONH with CASPT2/AVXZ and single point MRCI+Q calculations with fixed reference function (kcal mol^{-1})

	$\Delta E_5^{\ddagger}$	ΔE_{5rxn}
CASPT2/		
AVDZ	56.97	32.56
AVTZ	57.40	29.44
AVQZ	58.07	29.64
AV5Z	58.19	29.45
CBS	58.30	29.29
ZPE	-2.66	-1.59
CBS+ZPE	55.64	27.70
MRCI+Q/		
AVQZ//CASPT2/AVQZ	55.57	25.31
CCSD(T)/		
AVQZ	53.31	26.03
AVQZ+Q	51.54	26.77

Table S4 Calculated activation energies and energies for reactions represented on Figure 2

	$\Delta E_1^{\ddagger}$	ΔE_{1rxn}	$\Delta E_2^{\ddagger}$	ΔE_{2rxn}	$\Delta E_3^{\ddagger}$	ΔE_{3rxn}	$\Delta E_4^{\ddagger}$	ΔE_{4rxn}	$\Delta E_5^{\ddagger}$	ΔE_{5rxn}	$\Delta E_6^{\ddagger}$	ΔE_{6rxn}
CCSD(T)/												
AVDZ	8.08	1.05	31.66	4.46	11.95	0.05	50.85	-1.07	52.20	29.27	53.96	4.48
AVTZ	8.62	0.97	30.21	2.65	12.23	0.13	50.03	-1.54	52.68	26.19	52.39	2.21
AVQZ	8.85	0.93	29.92	2.30	12.56	0.25	50.25	-1.68	53.31	26.28	52.25	1.81
AV5Z	8.93	0.91		2.16		0.28		-1.58		26.03		1.77
AV5Z // AVQZ	8.93	0.91	29.77	2.16	12.60	0.28	50.33	-1.58	50.45	26.03	52.22	1.77
CBS	8.97	0.90		2.08		0.30		-1.52		25.88		1.75
CBS_{Q5sp}	9.00	0.89	29.62	2.01	12.65	0.31	50.40	-1.48	47.46	25.77	52.19	1.73
CBS_{TQ}	9.02	0.91	29.72	2.04	12.80	0.34	50.41	-1.77	53.77	26.34	52.15	1.52
ΔQ	0.54	0.10	0.31	0.83	0.17	-0.04	1.03	-0.43	-1.77	0.74	-0.41	0.47
ΔCV	0.11	-0.01	-0.08	-0.11	0.04	-0.02	0.01	-0.15	0.29	0.31	-0.21	-0.29
ΔSR	-0.09	0.00	-0.13	-0.29	-0.04	0.00	0.03	0.10	-0.19	0.05	-0.15	-0.20
ΔZPE	-0.83	-0.10	-1.27	2.30	-1.16	0.05	-3.69	0.67	-1.84	-0.71	-2.53	2.93
CBS + CORR	9.52	1.00		2.51		0.24		-2.01		26.98		1.73
CBS_{Q5sp}+CORR	9.55	0.99	29.72	2.44	12.81	0.25	49.42	-1.97	45.50	26.87	51.42	1.71
CBS_{TQ}+CORR	9.57	1.00	29.82	2.47	12.96	0.28	49.43	-2.26	52.11	27.45	51.38	1.50
CBS+CORR+ZPE	8.69	0.90		4.81		0.29		-1.34		26.27		4.66
CBS_{Q5sp}+CORR+ZPE	8.72	0.89	28.45	4.74	11.65	0.30	45.73	-1.29	43.95	26.16	48.89	4.65
CBS_{TQ}+CORR+ZPE	8.74	0.91	28.55	4.78	11.80	0.33	45.74	-1.59	50.26	26.74	48.84	4.43
PBE0/def2-TZVPPD												
E_{elec}	11.06	1.07	29.93	4.27	15.26	0.84	48.43	-4.88	61.04	28.95	50.40	1.30
E_{elec}+ZPE	10.25	0.88	28.72	6.66	14.05	0.93	44.82	-4.34	59.20	28.40	47.93	4.14
CBS-QB3												
E_{elec}	8.66	1.13	30.09	1.80	12.31	0.01	50.13	-2.34	53.98	27.72	51.48	0.60
E_{elec}+ZPE	7.91	0.99	28.84	4.13	11.09	0.09	46.55	-1.76	52.13	26.97	48.78	3.45

Table S5 Calculated T_1 and D_1 coupled cluster diagnostics for TS8, hypervalent intermediate and TS9 for reaction cyclic structure with H_2S at CCSD(T)/AVTZ, see Figure 5

structure	T_1	D_1
TS8	0.019	0.063
intermediate	0.021	0.061
TS9	0.029	0.121

Table S6 Calculated energy difference of *cis*-HSNO, *cis*-HONS, *trans*-HONS, SN(H)O and *cycl*-SONH with reference to *trans*-HSNO ((kcal mol^{-1})

	cis-HSNO	*cis*-HONS	*trans*-HONS	*SN(H)O*	*cycl*-SONH
CCSD(T)/					
AVDZ	-1.05	-5.51	-5.55	-4.48	-33.75
AVTZ	-0.97	-3.62	-3.75	-2.21	-28.39
AVQZ	-0.93	-3.23	-3.49	-1.81	-28.09
AV5Z	-0.91	-3.07	-3.35	-1.77	-27.80
AV5Z // AVQZ	-0.91	-3.07	-3.35	-1.77	-27.80
CBS	-0.90	-2.98	-3.27	-1.75	-27.63
CBS_{Q5sp}	-0.89	-2.91	-3.21	-1.73	-27.50
CBS_{TQ}	-0.91	-2.95	-3.29	-1.52	-27.86
ΔQ	-0.10	-0.93	-0.89	-0.47	-1.21
ΔCV	0.01	0.12	0.14	0.29	-0.02
ΔSR	0.00	0.29	0.29	0.20	0.14
ΔZPE	0.10	-2.21	-2.26	-2.93	-2.22
CBS+CORR	-1.00	-3.50	-3.74	-1.73	-28.71
CBS_{Q5sp}+CORR	-0.99	-3.43	-3.68	-1.71	-28.58
CBS_{TQ}+CORR	-1.00	-3.48	-3.76	-1.50	-28.95
CBS+CORR+ZPE	-0.90	-5.71	-6.00	-4.66	-30.94
CBS_{Q5sp}+CORR+ZPE	-0.89	-5.64	-5.94	-4.65	-30.81
CBS_{TQ}CORR+ZPE	-0.91	-5.68	-6.02	-4.43	-31.17
PBE0/def2-TZVPPD					
E_{elec}	-1.07	-5.35	-6.18	-1.30	-30.25
E_{elec}+ZPE	-0.88	-7.55	-8.48	-4.14	-32.54
CBS-QB3					
E_{elec}	-1.13	-2.93	-2.94	-0.60	-28.33
E_{elec}+ZPE	-0.99	-5.11	-5.21	-3.45	-30.42

Table S7 Calculated energy of water assisted reaction with CBS-QB3 (kcal/mol), see Figure 3

	one water molecule		
	$\Delta E_2^{\ddagger}$	ΔE_{2rxn}	E_{form} (cisHSNO)
Eelec	16.21	-0.58	-4.77
ΔZPE	-0.78	2.43	2.10
Eelec+ΔZPE	15.43	1.85	-2.67
	two water molecules		
Eelec	15.30	-0.88	-12.52
ΔZPE	-0.68	2.29	4.63
Eelec+ΔZPE	14.62	1.42	-7.89

	one water molecule		
	$\Delta E_4^{\ddagger}$	ΔE_{4rxn}	$E_{\mathbf{form}}$ (planar cyclo)
Eelec	25.08	-1.74	-6.08
ΔZPE	-2.52	0.30	1.72
Eelec+ΔZPE	22.55	-1.43	-4.36
	two water molecules		
Eelec	18.66	-1.51	-17.44
ΔZPE	-3.49	0.24	4.67
Eelec+ΔZPE	15.16	-1.27	-12.78

	one water molecule		
	$\Delta E_6^{\ddagger}$	ΔE_{6rxn}	$E_{\mathbf{form}}$ (transHSNO)
Eelec	23.53	-2.47	-4.55
ΔZPE	-0.50	2.62	2.08
Eelec+ΔZPE	23.03	0.16	-2.47
	two water molecules		
Eelec	16.35	-4.14	-13.40
ΔZPE	-1.12	2.58	4.93
Eelec+ΔZPE	15.23	-1.57	-8.47

Table S8 Calculated energies for reaction, H_2S +*cycl*-SONH → HSSH +HNO, without and with one water molecule with CBS-QB3 (kcal/mol (Sheme 1B).

	$\Delta E^{\ddagger}$	$\Delta E+ZPE^{\ddagger}$	ΔE_{rxn}	$\Delta E_{rxn}+ZPE$
0 water	31.37	31.52	12.73	15.21
1 water	31.46	29.87	16.77	17.18

Supplementary Figures S1-S2

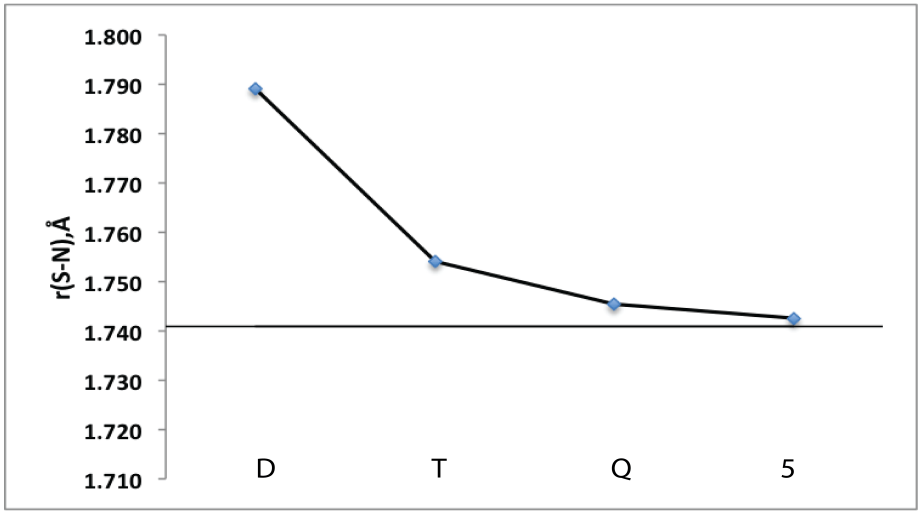

Figure S1 Calculated bond length [*r*(S–N)] vs AVxZ basis set size of cyclic isomer cycl-SONH.

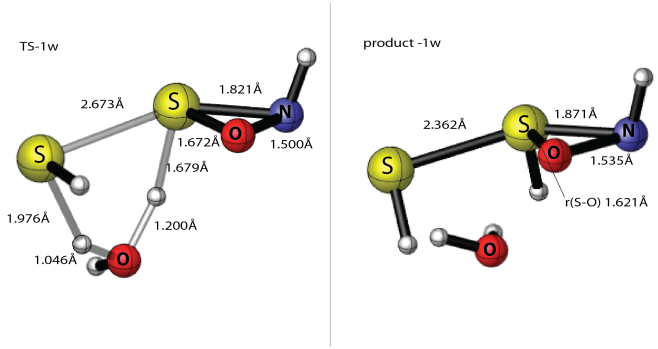

Figure S2 Geometries of transition state and product for water-assisted reaction H_2S + *cycl*-SONH → HSSH +HNO (Scheme 1B) calculated with CBS-QB3

Cartesian Coordinates and Energies

Cartezian coordinates and energy for molecules calculated
CCSD(T)/AV5Z trans-HSNO E = -528.12907128 Hartree
Coordinates in ang:

O	-1.5357804925	0.3000146963	0.0000000000
N	-0.6984754913	-0.5321015376	0.0000000000
S	1.0241603160	0.1182397496	0.0000000000
H	1.5083470692	-1.1288716575	0.0000000000

CCSD(T)/AV5Z cis-HSNO E = -528.114059705869 Hartree
Coordinates in ang:

O	-2.872597887	-0.583657461	0.000000000
N	-1.309067404	1.017638577	0.000000000
S	1.961890107	-0.073214538	0.000000000
H	1.386352570	2.548099085	0.000000000

CCSD(T)/AV5Z cis-HONS E=-528.12417552 Hartree
Coordinates in ang:

S	0.0000000000	0.1064223692	-0.9812901234
N	0.0000000000	-0.5930290763	0.4380707411
O	0.0000000000	0.2335472164	1.5095827570
H	0.0000000000	1.1487428531	1.1625866079

CCSD(T)/AV5Z trans-HONS E=- 528.12372977 Hartree
Coordinates in ang:

S	0.0000000000	0.1061888973	-0.9885548783
N	0.0000000000	-0.5855918710	0.4238309431
O	0.0000000000	0.3163300720	1.4685369115
H	0.0000000000	-0.2612236265	2.2430770350

CCSD(T)/AV5Z Y-isomer E= -528. 126248980 Hartree
Coordinates in ang:

S	1.0199555328	-0.1166787662	-0.0001458936
N	-0.5099302497	0.4210572459	0.0067015761
O	-1.5630520150	-0.2235702637	0.0043321045
H	-0.6253846686	1.4416086670	0.0140056740

CCSD(T)/AV5Z cycl-SONH E= -528.084774910 Hartree
Coordinates in ang:

H	0.0391063657	-0.2897303125	0.2391131160
N	-0.0065204147	0.4849644544	0.9104906808
O	0.7696630627	-0.0338395631	2.0410878810
S	-0.9021495334	-0.1611532553	2.2584518070

CCSD(T)/AV5Z TS1 E= -528.11484674 Hartree
Coordinates in ang:

S	-0.0411292716	0.0618952422	-1.1054157887
N	0.0089515410	-0.5409316049	0.8166548809
O	-0.0070901069	0.3404651777	1.5667621663
H	1.2963672005	0.1439239262	-1.0578648915

CCSD(T)/AVQZ TS2 E= -528.06488612 Hartree
Coordinates in ang:

S	2.8775787706	3.0401700755	0.2929143367
N	4.4365715347	2.9650008640	-0.2252834565
O	4.3995258542	2.9499369591	-1.4962397132

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H          3.0415008405        3.0115661015       -1.3381051669

CCSD(T)/AVQZ TS3 E= -528.08889419 Hartree
Coordinates in ang:
S            1.0071390000       -0.1339430000        0.0007030000
N           -0.3600090000        0.6337620000        0.0394570000
O           -1.5028280000       -0.2281200000       -0.1268210000
H           -1.7038200000       -0.5282320000        0.7694400000

CCSD(T)/AVQZ TS4 E= -528.02842194 Hartree
Coordinates in ang:
S            -0.0000001685        0.0894168163       -1.0289924232
N             0.0000009202       -0.4701751379        0.4494352665
O            -0.0000000326        0.2930088909        1.5731932525
H            -0.0000069095       -0.9614336905        1.5122368552

CCSD(T)/AVQZ TS5 E= -528.026223040 Hartree
Coordinates in ang:
S          1.0095694125       -0.1484011750       -0.0425098804
N         -0.5759113042        0.5136705597        0.0938371179
O         -1.0651446333       -0.7234416325       -0.0310633856
H         -0.8497154749        1.1355622478       -0.6749568519

CCSD(T)/AVQZ TS6 E= -528.030775640 Hartree
Coordinates in ang:
S           -1.2213442637        -0.0714178072        1.92911803643
N            0.3359923759         0.1613495133        1.24400186468
O            1.3937918157         0.0691072543        1.83230319440
H           -0.6083829278        -0.1590249603        0.44347590450

CBS-QB3 TS2 E=-527.302774 Hartree
Coordinates in ang:
 S     0.082357     0.000000     1.246674
 N     1.702890     0.000000     1.555431
 O     2.291651     0.000000     0.442085
 H     1.030974     0.000000    -0.117104

CBS-QB3 TS2-1w E=-603.386248 Hartree
Coordinates in ang:
 O    -0.424796     1.396624    -0.007671
 N     0.749826     0.970914     0.027831
 S     1.031874    -0.702093     0.000296
 H    -0.686244    -1.047037    -0.062699
 O    -1.758500    -0.649572    -0.094212
 H    -2.208346    -0.859718     0.737104
 H    -1.397807     0.367430    -0.058907

CBS-QB3 TS2-2w E=-679.454062 Hartree
Coordinates in ang:
 O     1.121103    -0.978661     0.088991
 S     0.449572     1.905418    -0.130258
 N    -1.235458     2.023306    -0.001835
 O    -1.942315     1.004811     0.091903
 O    -1.222120    -1.418324    -0.087226
 H     0.983106     0.074839     0.003059
 H     1.479566    -1.157845     0.968105
 H     0.003335    -1.326237    -0.000376
 H    -1.537100    -0.430864    -0.002078
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 H    -1.524178    -1.757915    -0.937512

CBS-QB3 TS4 E=-527.254492 Hartree
Coordinates in ang:
 S     1.055531    -0.081849     0.000159
 N    -0.439759     0.438750    -0.000868
 O    -1.537429    -0.334925     0.000037
 H    -1.510749     0.917733     0.003239

CBS-QB3 TS4-1w E=-603.366061 Hartree
Coordinates in ang:
 S    -1.674107    -0.227933     0.005940
 N    -0.081168    -0.045539    -0.010517
 O     0.498421     1.104041     0.014214
 O     2.228610    -0.486753    -0.097812
 H     1.745200     0.524836    -0.030147
 H     2.667118    -0.704389     0.733250
 H     1.125325    -0.793045    -0.055738

CBS-QB3 TS4-2w E=-679.446363 Hartree
Coordinates in ang:
 S    -0.128198    -0.124000    -0.112648
 N     0.139561    -0.029245     1.480369
 O     1.304674     0.218341     1.946243
 H     1.182852     0.247859     3.354747
 O     0.832036     0.214477     4.373205
 H     1.267776    -0.512694     4.831011
 H    -0.335551    -0.016734     4.128639
 H    -0.892674    -0.195540     2.537984
 O    -1.348074    -0.247755     3.522300
 H    -2.012689     0.445292     3.605822

CBS-QB3 TS6 E=-527.263246 Hartree
Coordinates in ang:
 S    -1.226508    -0.066305     1.929187
 N     0.355304     0.052078     1.250304
 O     1.399471     0.127716     1.837025
 H    -0.628210    -0.113476     0.432383

CBS-QB3 TS6-1w E=-603.373361 Hartree
Coordinates in ang:
 O     0.613886     0.242882     4.387097
 S     1.621199     0.349550     1.812539
 N    -0.044799    -0.092511     2.054794
 O    -0.796225    -0.340966     1.152457
 H     1.405877     0.411257     3.612369
 H     0.826496    -0.562080     4.879546
 H    -0.056189    -0.008814     3.555196

CBS-QB3 TS6-2w E=-679.451568 Hartree
Coordinates in ang:
 O    -0.297689    -0.181349     0.117193
 N     0.022429    -0.052040     1.275924
 S     1.648291     0.373830     1.688978
 H     1.263114     0.307806     3.540132
 O     0.788626     0.178816     4.493088
 H     1.171634    -0.606884     4.904027
 H    -0.307418    -0.026290     4.132456
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 H    -0.935265    -0.205926     2.494833
 O    -1.339555    -0.240610     3.470114
 H    -2.004454     0.452649     3.550928

UPBE0/def2-TZVPPD TS7 E=-927.683957 Hartree
Coordinates in ang:
 S     2.050949     0.036867     0.783478
 N     0.510799     0.056504     0.091777
 O     0.263399     0.416896    -1.071774
 H    -0.187354    -0.492086     0.595843
 S     3.752629    -1.936314    -0.524466
 H     2.753113     0.056403    -0.387802
 H     4.570579    -1.638557     0.500230

UPBE0/def2-TZVPPD TS7-1w E=-1004.084809 Hartree
Coordinates in ang:
 S    -2.064693    -0.558907     0.401619
 O    -0.663658     1.951122    -0.106829
 S     0.438422    -0.581806    -0.583081
 N     1.986234    -0.528274     0.030565
 O     2.536967     0.410800     0.613620
 H     2.405488    -1.458189     0.157903
 H    -2.475351    -0.874288    -0.838255
 H    -1.448429     1.322070     0.100234
 H    -0.885825     2.463954    -0.890309
 H     0.052304     0.971333    -0.396625

UPBE0/def2-TZVPPD TS7-2w E=-1080.491881 Hartree
Coordinates in ang:
 O     0.348157     0.946860    -0.311663
 H    -0.092877    -0.226455     1.154478
 N     0.674946     0.151247     0.584160
 S     2.078456    -0.754922     0.675865
 H     3.361003    -3.327276     0.808057
 S     3.124020    -2.816164    -0.409082
 O     3.517772     0.543563    -1.408570
 H     3.716706     1.458998    -1.192495
 H     2.870981     0.074117    -0.547990
 H     4.383809    -0.017839    -1.458081
 O     5.453915    -1.048045    -1.349882
 H     5.815554    -1.394354    -2.168267
 H     4.888500    -1.776094    -0.967890

CCSD(T)/AVTZ TS8 E=-926.914656 Hartree
Coordinates in ang:
 S    -2.303620     0.505995     4.191903
 S    -1.240751    -0.344113     1.986262
 H    -1.577621    -0.945121     3.245591
 H    -1.081492     0.634971     4.734929
 N     0.357067    -0.775913     1.303435
 O     0.195684     0.306255     2.384535
 H     0.458736    -0.205102     0.452123

CCSD(T)/AVTZ HSS(H)ONH intermediate E=-926.943808656 Hartree
Coordinates in ang:
 S          0.0047583231        0.0886938617       -1.8100885144
 S          0.0927697768       -0.5219386904        0.3571794483
 O          0.0744511421        0.9486934912        0.9756381707
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N	-0.1887846834	-0.0690302771	2.1304292442
H	-1.1912843730	-0.9105526793	0.2808530925
H	-1.2048400371	0.6674891119	-1.7378311074
H	0.7356346385	-0.0762124331	2.5784297072

CCSD(T)/AVTZ TS9 Energy=-926.930491795 Hartree
Coordinates in ang:

S	-0.0023141458	0.0714725034	-2.0045305889
S	0.1198147432	-0.3262333275	0.2255994400
N	-0.2033531980	-0.3148030494	2.3119673634
O	0.0530132991	0.8260454635	1.4845115650
H	-1.1997968327	-0.5313640580	0.2263776281
H	-1.2922744231	0.4419250407	-1.9972806891
H	0.7390473734	-0.5447732320	2.6620325234