Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Biological Control of *S*-Nitrosothiol Reactivity: The Potential Role of Sigma-Hole Interactions

Niloufar Hendinejad and Qadir K. Timerghazin*

Department of Chemistry, Marquette University, PO Box 1881, Milwaukee, WI 53201-1881, United States
E-mail: qadir.timerghazin@marquette.edu

Supporting Information

Supporting Figures

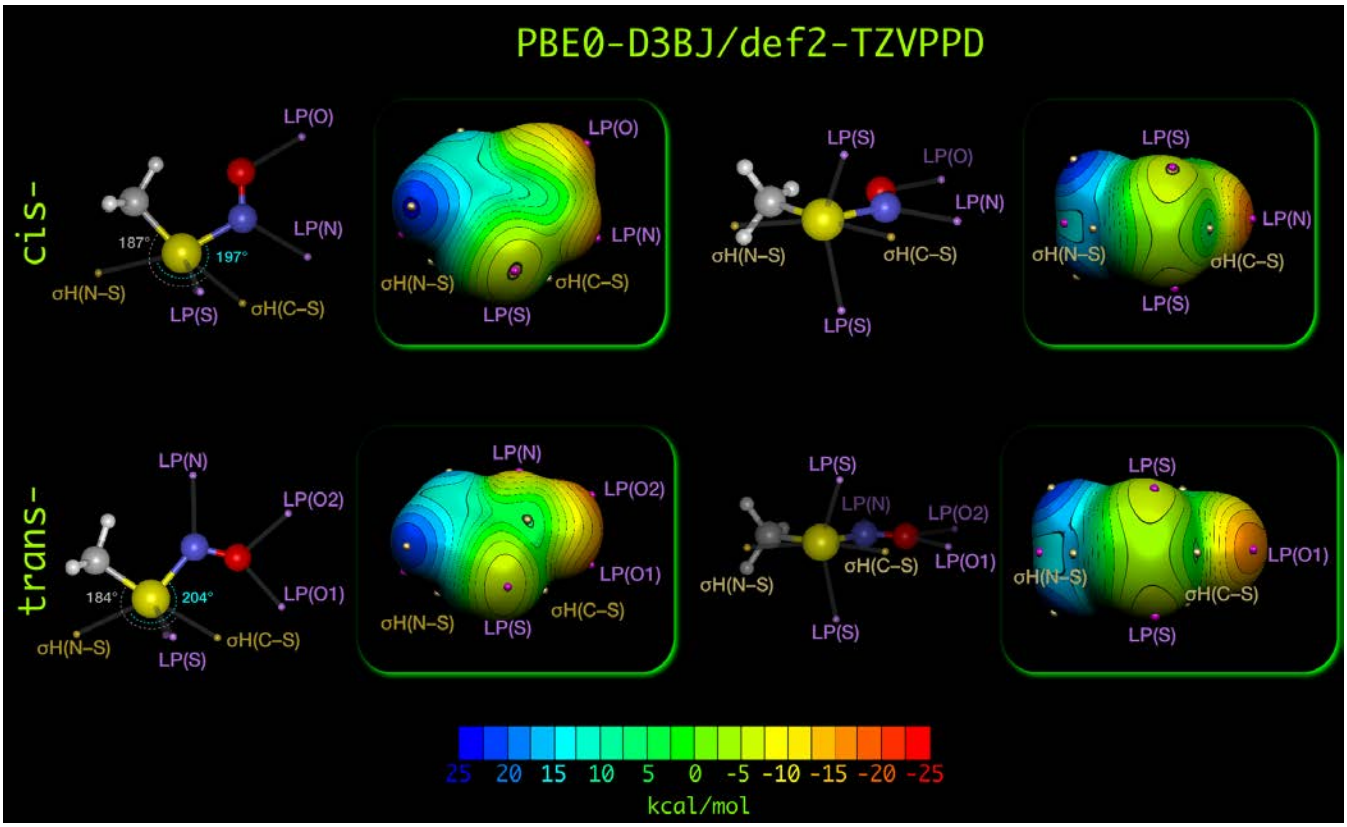

Fig. S1. Top and side views of the molecular electrostatic potential (MEP) of *cis*- and *trans*-CH_3SNO calculated at the PBE0-D3BJ/def2-TZVPP level mapped onto the electron density isosurface (0.001 au). Surface MEP minima ($V_{S,min}$) and maxima ($V_{S,max}$) are shown as purple and golden dots, respectively. Reference molecular geometries with select relevant $V_{S,min}$ and $V_{S,max}$ points are shown left of the corresponding MEP maps.

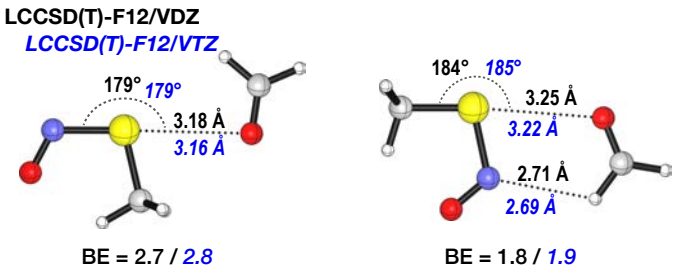

Fig. S2. Comparative geometry studied of *cis*-CH_3SNO binary complexes with formaldehyde in gas phase within LCCSD(T)-F12/VDZ and LCCSD(T)-F12/VTZ.

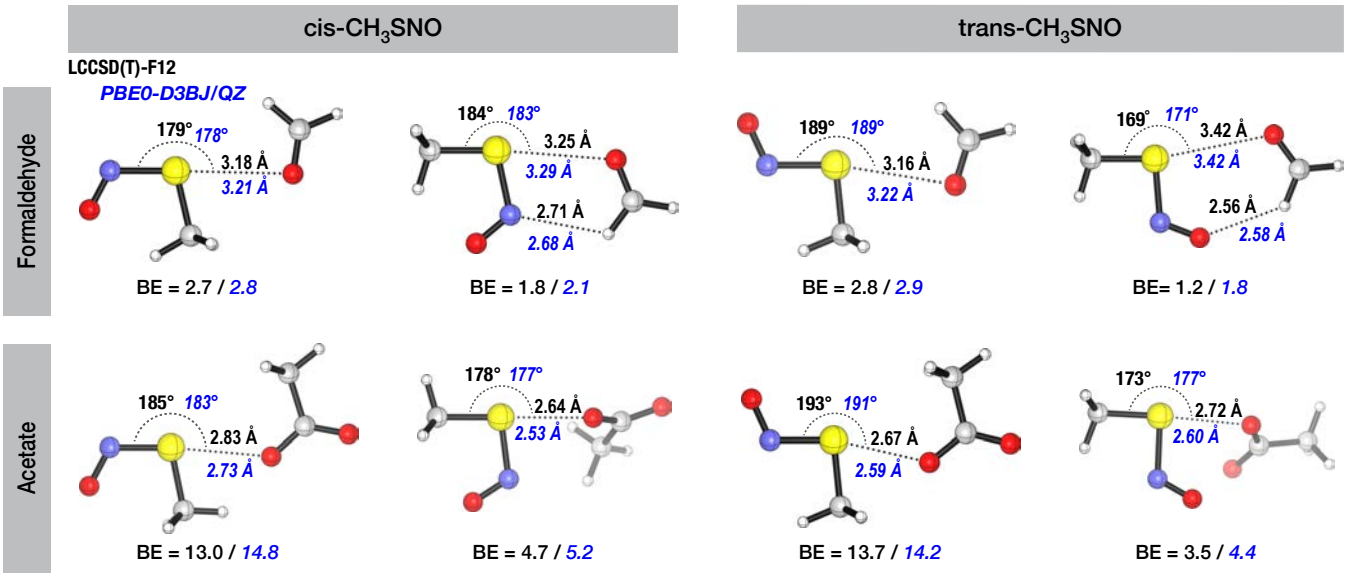

Fig. S3. σ-Hole bound complexes of CH_3SNO with formaldehyde, acetate with relevant geometric parameters and binding energies (*BE*) calculated with LCCSD(T)-F12/VDZ-F12 (black typeface) and PBE0-D3BJ/def2-QZVPP (blue typeface).

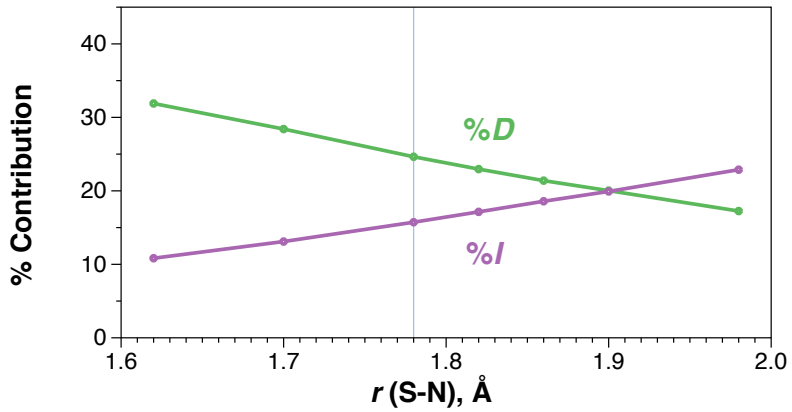

Fig. S4. Natural Resonance Theory weights vs S–N bond length in *cis*-CH_3SNO molecule. Blue line shows the equilibrium S–N distance.

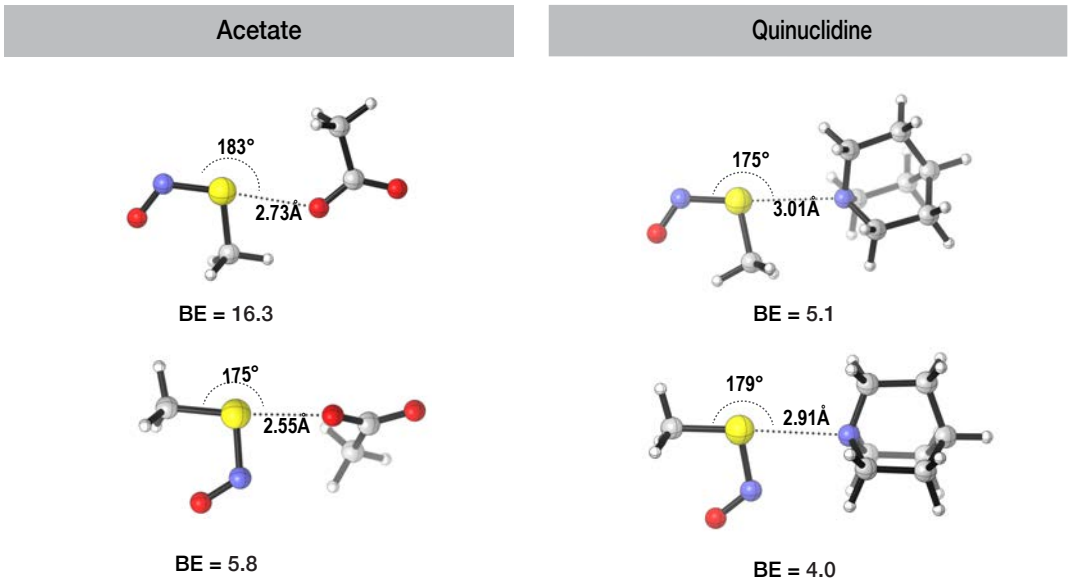

Fig. S5. σ-Hole bound complexes of *cis*-CH_3SNO with shortened S–N bond (1.65 Å) with acetate and quinuclidine with relevant geometric parameters and binding energies (*BE*) in the gas phase calculated within PBE0-D3BJ/def2-TZVPPD.

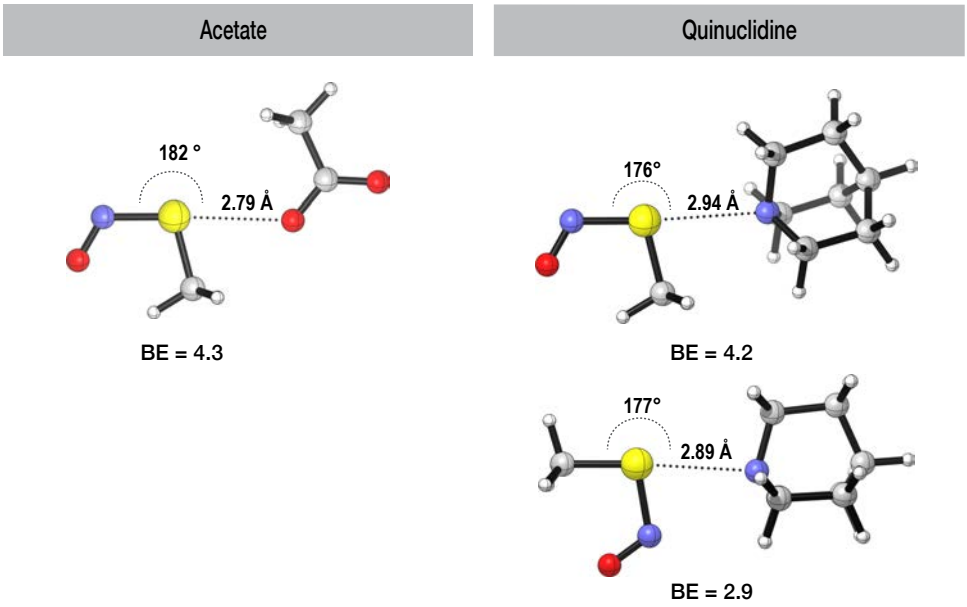

Fig. S6. σ-Hole bound complexes of *cis*-CH_3SNO with acetate and quinuclidine with relevant geometric parameters and binding energies (*BE*) in diethylether calculated within PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD

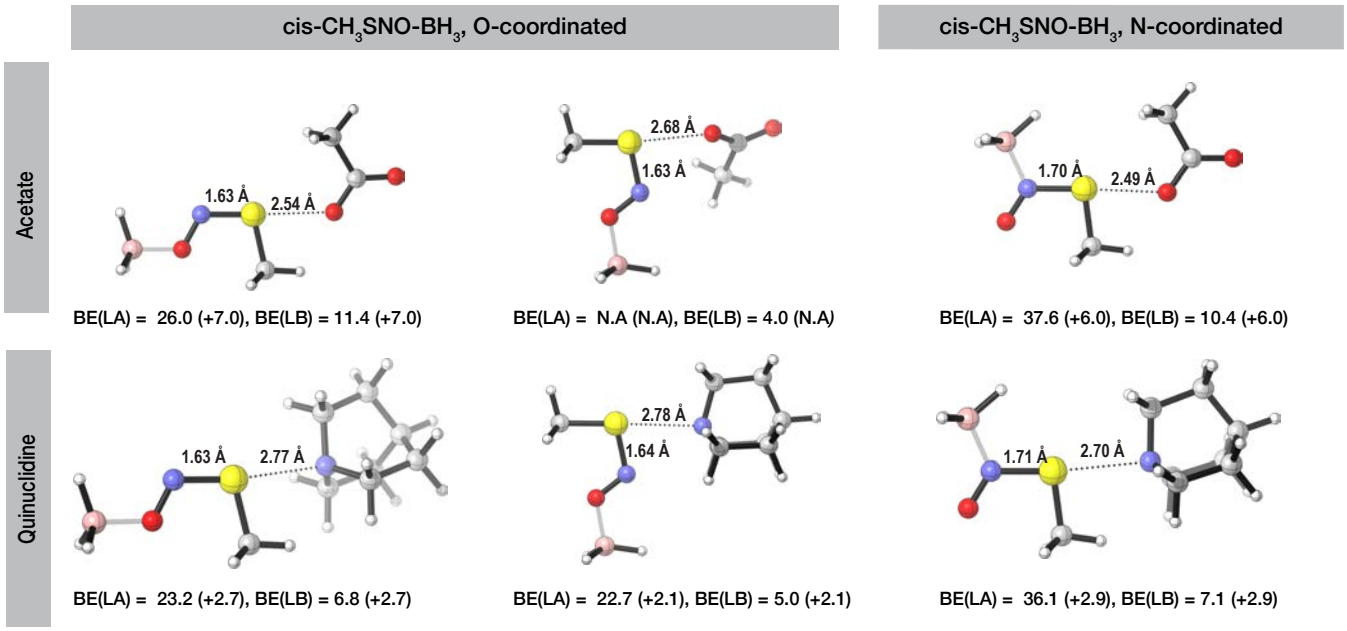

Fig. S7. σ-Hole bound complexes of *cis*-CH_3SNO with acetate and quinuclidine as Lewis bases and borane as Lewis acid with relevant geometric parameters and binding energies (*BE*) calculated with PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD. The values in parenthesis indicate enhancement of the binding energies with respect to the binary complexes.

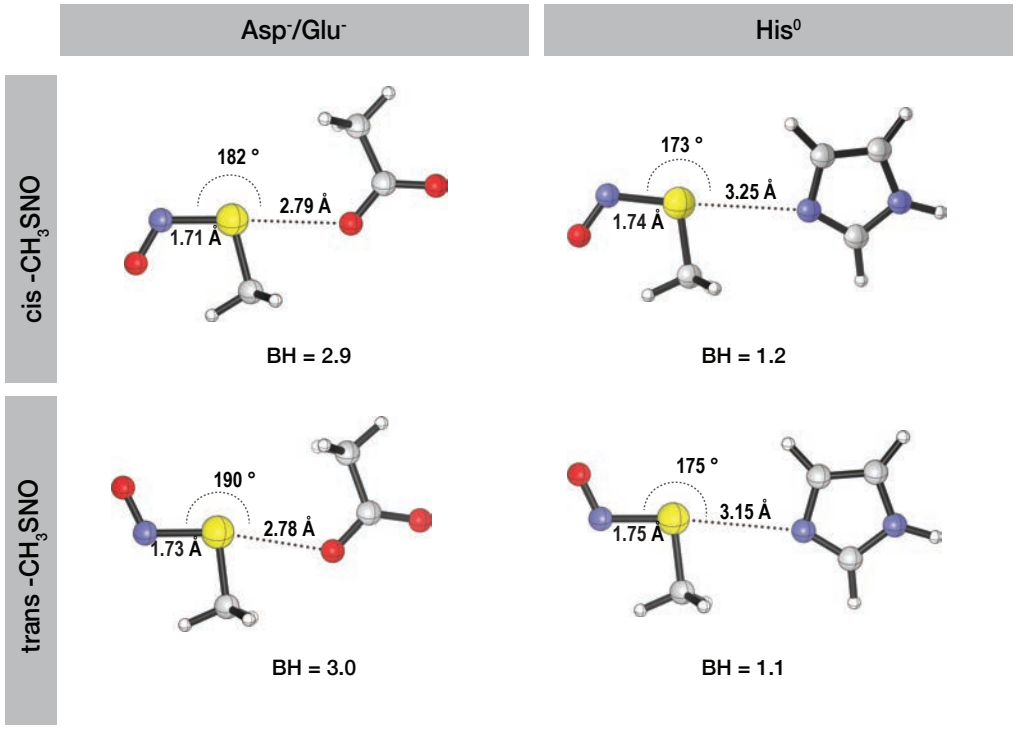

Fig. S8. σ-Hole bound complexes of *cis*- and *trans*-CH_3SNO with Asp^-/Glu^- and His^0 models as Lewis bases at CH_3SNO sulfur, with relevant geometric parameters and binding enthalpies (*BH*) calculated with PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD.

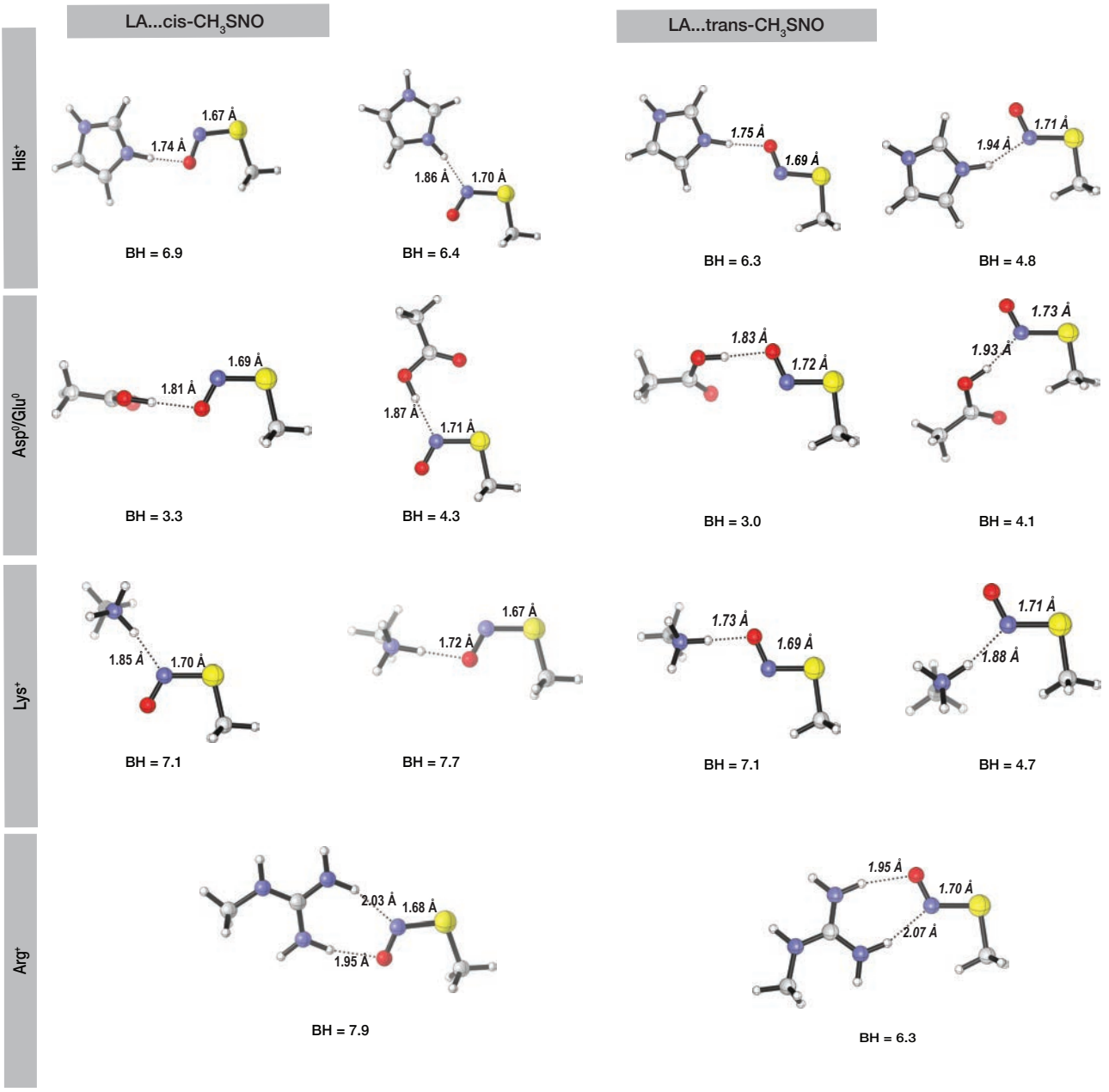

Fig. S9. σ-Hole bound complexes of *cis*- and *trans*-CH_3SNO with His^0, Asp^0/Glu^0, Lys^+ and Arg^+ models as Lewis acids with relevant geometric parameters and binding enthalpies (*BH*) calculated with PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD.

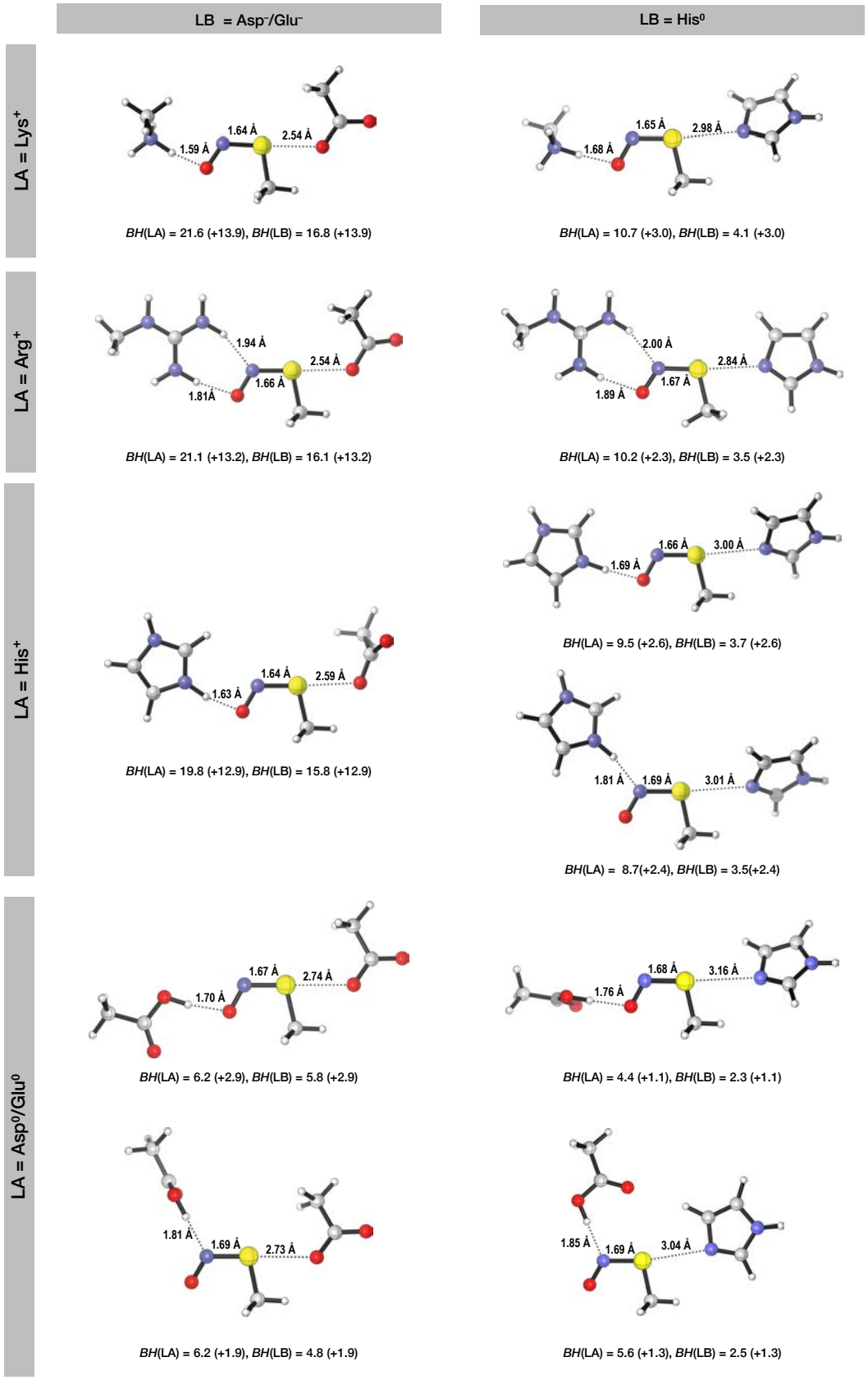

Fig. S10. σ-Hole bound ternary complexes of *cis*-CH_3SNO with His^+, Asp^0/Glu^0, Lys^+ and Arg^+ models as Lewis acids and His^0, Asp^- /Glu^- models with relevant geometric parameters and binding enthalpies (*BH*) calculated with PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD. The values in parenthesis indicate enhancement of the binding energies with respect to the binary complexes.

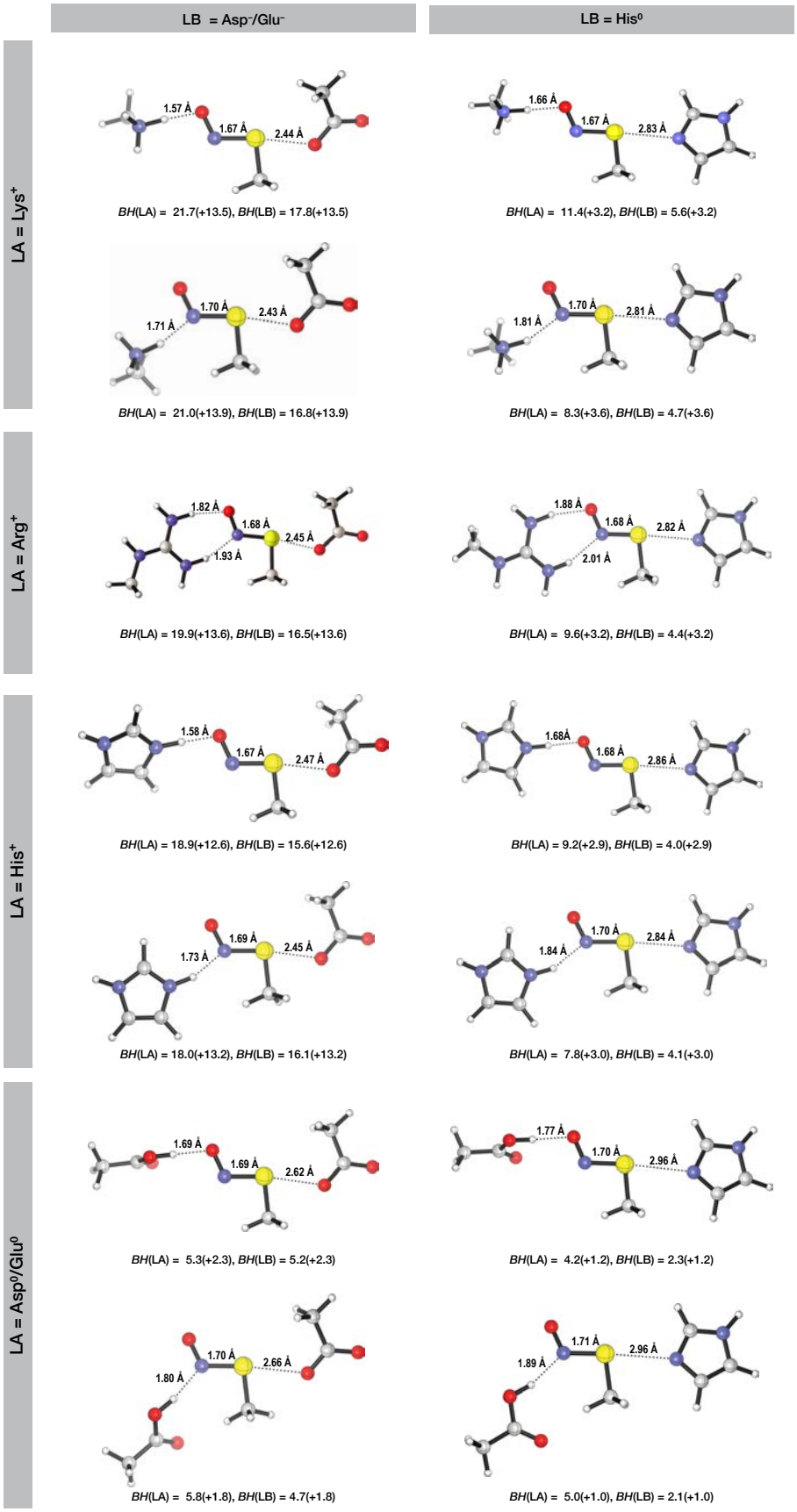

Fig. S11. σ-Hole bound ternary complexes of *trans*-CH_3SNO with models of His^+, Asp^0/Glu^0, Lys^+ and Arg^+ as Lewis acids and models of His^0, Asp^-/Glu^- with relevant geometric parameters and binding enthalpies (*BH*) calculated with PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD. The values in parenthesis indicate enhancement of the binding energies with respect to the binary complexes.

Supporting Tables

Table S1. LB–S intermolecular bond lengths in σ-Hole bound CH_3SNO complexes (in Å); PBE0- D3BJ/def2-TZVPPD calculations.

Complex	N-S or C-S	BH_3 at O or N	LB···S Interaction	$r(Y\cdots S)$
cis-CH_3SNO-CH_2O	N-S		O···S	3.216
cis-CH_3SNO-CH_2O	C-S		O···S	3.298
cis-CH_3SNO-acetate	N-S		O···S	2.734
cis-CH_3SNO-acetate	C-S		O···S	2.537
cis-CH_3SNO-quinuclidine	N-S		O···S	3.036
cis-CH_3SNO-quinuclidine	C-S		O···S	2.869
trans-CH_3SNO-CH_2O	N-S		O···S	3.232
trans-CH_3SNO-CH_2O	C-S		O···S	3.412
trans-CH_3SNO-acetate	N-S		O···S	2.595
trans-CH_3SNO-acetate	C-S		O···S	2.605
trans-CH_3SNO-quinuclidine	N-S		S···N	3.029
trans-CH_3SNO-quinuclidine	C-S		S···N	2.992
cis-CH_3SNO-BH_3-acetate	N-S	O	O···S	2.422
cis-CH_3SNO-BH_3-acetate	C-S	O	O···S	2.373
cis-CH_3SNO-BH_3-acetate	N-S	N	O···S	2.365
cis-CH_3SNO-BH_3-quinuclidine	N-S	O	N···S	2.883
cis-CH_3SNO-BH_3-quinuclidine	C-S	O	N···S	2.774
cis-CH_3SNO-BH_3-quinuclidine	N-S	N	N···S	2.813
cis-CH_3SNO*-acetate	N-S		O···S	2.732
cis-CH_3SNO*-acetate	C-S		O···S	2.553
cis-CH_3SNO*-quinuclidine	N-S		N···S	3.007
cis-CH_3SNO*-quinuclidine	C-S		N···S	2.906

Table S2. Thermodynamic parameters of the binary and ternary *cis*-CH_3SNO complexes with BH_3 as Lewis acid and acetate and quinuclidine as Lewis bases in σ-hole bound CH_3SNO complexes in the gas phase; PBE0-D3BJ/def2-TZVPPD calculations.

Complex	N-S or C-S	LA at O or N	LB···S Interaction	LA…S Binding energy(kcal/mol)				LB…S Binding energy(kcal/mol)				Energy Enhancement			
				ΔE_e	ΔE_0	ΔH	ΔG	ΔE_e	ΔE_0	ΔH	ΔG	ΔE_e	ΔE_0	ΔH	ΔG
cis-CH_3SNO-BH_3		O		-16.39	-12.83	-35.91	-24.30								
cis-CH_3SNO-BH_3		N		-31.05	-27.06	-50.22	-38.80								
cis-CH_3SNO-acetate	N-S		O…S					-14.81	-13.90	-13.42	-4.46				
cis-CH_3SNO-acetate	C-S		O…S					-5.27	-4.49	-4.16	+6.31				
cis-CH_3SNO-quinuclidine	N-S		N…S					-4.56	-3.98	-3.21	4.54				
cis-CH_3SNO-quinuclidine	C-S		N…S					-3.83	-3.24	-2.55	6.24				
cis-CH_3SNO-BH_3-acetate	N-S	O	O…S	-30.69	-26.72	-49.97	-37.59	-29.11	-27.79	-27.48	-17.75	-14.30	-13.89	-14.06	-13.29
cis-CH_3SNO-BH_3-acetate	C-S	O	O…S	-26.82	-22.97	-46.20	-33.95	-15.70	-14.63	-14.44	-3.34	-10.43	-10.14	-10.28	-9.65
cis-CH_3SNO-BH_3-acetate	N-S	N	O…S	-42.10	-37.57	-61.03	-47.44	-25.87	-24.40	-24.23	-13.10	-11.06	-10.51	-10.81	-8.64
cis-CH_3SNO-BH_3-quinuclidine	N-S	O	N…S	-19.36	-15.61	-38.72	-26.96	-7.53	-6.76	-6.01	1.87	-2.97	-2.78	-2.80	-2.66
cis-CH_3SNO-BH_3-quinuclidine	C-S	O	N…S	-19.47	-15.63	-38.82	-26.39	-6.91	-6.03	-5.46	4.15	-3.08	-2.80	-2.91	-2.09
cis-CH_3SNO-BH_3-quinuclidine	N-S	N	N…S	-34.02	-29.80	-53.04	-40.81	-7.54	-6.72	-6.03	2.52	-2.98	-2.74	-2.81	-2.02

Table S3. LA–S intermolecular bond lengths in σ-hole bound CH_3SNO complexes (in Å).

Complex	N-S or C-S	BH_3 at O or N	r(B–X)
cis-CH_3SNO-BH_3		O	1.586
cis-CH_3SNO-BH_3		N	1.557
cis-CH_3SNO-BH_3-acetate	N-S	O	1.569
cis-CH_3SNO-BH_3-acetate	C-S	O	1.575
cis-CH_3SNO-BH_3-acetate	N-S	N	1.568
cis-CH_3SNO-BH_3-quinuclidine	N-S	O	1.581
cis-CH_3SNO-BH_3-quinuclidine	C-S	O	1.586
cis-CH_3SNO-BH_3-quinuclidine	N-S	N	1.559

PCM(ε=4.2)

Table S4. Thermodynamic parameters of the binary and ternary *cis*-CH_3SNO complexes with borane as Lewis acid and acetate and quinuclidine as Lewis bases in diethylether; PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD calculations.

Complex	N-S or C-S	LA at O or N	LB···S Interaction	LA…S Binding (kcal/mol)				LB…S Binding energy(kcal/mol)				Binding Enhancement			
				ΔE_e	ΔE_0	ΔH	ΔG	ΔE_e	ΔE_0	ΔH	ΔG	ΔE_e	ΔE_0	ΔH	ΔG
cis-CH_3SNO-BH_3		O		-20.54	-16.77	-17.99	-7.26								
cis-CH_3SNO-BH_3		N		-33.19	-28.99	-30.30	-19.47								
cis-CH_3SNO-acetate	N-S		O…S					-4.36	-3.30	-2.91	6.67				
cis-CH_3SNO-acetate	C-S		O…S	-	-	-	-	-	-	-	-	-	-	-	-
cis-CH_3SNO-quinuclidine	N-S		N…S					-4.15	-3.46	-2.78	5.59				
cis-CH_3SNO-quinuclidine	C-S		N…S					-2.89	-2.33	-1.67	7.17				
cis-CH_3SNO-BH_3-acetate	N-S	O	O…S	-27.58	-23.71	-25.00	-13.62	-11.40	-10.24	-9.92	0.31	-7.03	-6.94	-7.01	-6.37
cis-CH_3SNO-BH_3-acetate	C-S	O	O…S	-	-	-	-	-3.98	-3.08	-2.71	7.41	-	-	-	-
cis-CH_3SNO-BH_3-acetate	N-S	N	O…S	-39.20	-30.78	-33.16	-18.68	-10.36	-5.09	-5.77	7.47	-6.00	-1.79	-2.86	0.80
cis-CH_3SNO-BH_3-quinuclidine	N-S	O	N…S	-23.24	-19.35	-20.53	-9.87	-6.84	-6.04	-5.33	2.98	-2.69	-2.58	-2.54	-2.61
cis-CH_3SNO-BH_3-quinuclidine	C-S	O	N…S	-22.67	-18.75	-20.01	-8.70	-5.01	-4.32	-3.70	5.72	-2.12	-1.98	-2.03	-1.45
cis-CH_3SNO-BH_3-quinuclidine	N-S	N	N…S	-36.13	-31.74	-33.07	-21.65	-7.09	-6.21	-5.55	3.41	-2.93	-2.75	-2.77	-2.17

Table S5. Effect of a polarizable environment: S–N bond properties in σ-hole bound CH_3SNO complexes.

Complex	BH_3 at O or N	N-S or C-S	r(S-N)	Δr(S-N)
cis-CH_3SNO			1.757	
cis-CH_3SNO-quinuclidine		N-S	1.731	-0.026
cis-CH_3SNO-acetate		N-S	1.705	-0.052
cis-CH_3SNO-quinuclidine		C-S	1.749	-0.008
cis-CH_3SNO-BH_3	O		1.634	-0.124
cis-CH_3SNO-BH_3-quinuclidine	O	N-S	1.635	-0.122
cis-CH_3SNO-BH_3-acetate	O	N-S	1.630	-0.127
cis-CH_3SNO-BH_3-quinuclidine	O	C-S	1.639	-0.118
cis-CH_3SNO-BH_3-acetate	O	C-S	1.634	-0.123
cis-CH_3SNO-BH_3	N		1.698	-0.059
cis-CH_3SNO-BH_3-quinuclidine	N	N-S	1.707	-0.050
cis-CH_3SNO-BH_3-acetate	N	N-S	1.701	-0.056

Table S6. LB–S intermolecular bond lengths in σ-hole bound CH_3SNO complexes (in Å); PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD calculations.

Complex	N-S or C-S	BH_3 at O or N	LB···S Interaction	r(Y···S)
cis-CH_3SNO-acetate	N-S		O···S	2.790
cis-CH_3SNO-quinuclidine	N-S		O···S	2.940
cis-CH_3SNO-quinuclidine	C-S		O···S	2.889
cis-CH_3SNO-BH_3-acetate	N-S	O	O···S	2.539
cis-CH_3SNO-BH_3-acetate	C-S	O	O···S	2.684
cis-CH_3SNO-BH_3-acetate	N-S	N	O···S	2.492
cis-CH_3SNO-BH_3-quinuclidine	N-S	O	N···S	2.768
cis-CH_3SNO-BH_3-quinuclidine	C-S	O	N···S	2.780
cis-CH_3SNO-BH_3-quinuclidine	N-S	N	N···S	2.701

Table S7. BH_3–RSNO intermolecular bond lengths in σ-hole bound CH_3SNO complexes (in Å); PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD calculations.

Complex	N-S or C-S	BH_3 at O or N	r(B–X)
cis-CH_3SNO-BH_3		O	1.577
cis-CH_3SNO-BH_3		N	1.564
cis-CH_3SNO-BH_3-acetate	N-S	O	1.564
cis-CH_3SNO-BH_3-acetate	C-S	O	1.571
cis-CH_3SNO-BH_3-acetate	N-S	N	1.568
cis-CH_3SNO-BH_3-quinuclidine	N-S	O	1.571
cis-CH_3SNO-BH_3-quinuclidine	C-S	O	1.574
cis-CH_3SNO-BH_3-quinuclidine	N-S	N	1.565

Table S8. Thermodynamic parameters of the binary and ternary CH_3SNO complexes with Arg^+, His^+, Lys^+ and Asp^0/Glu^0 models as Lewis acid and His^0 and Asp^-/Glu^- models as Lewis bases; PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD calculations.

Complex	N-S or C-S	LA at O or N	LB···S Interaction	LA…O or N Binding energy(kcal/mol)				LB…S Binding energy(kcal/mol)				Enhancement			
				ΔE_e	ΔE_0	ΔH	ΔG	ΔE_e	ΔE_0	ΔH	ΔG	ΔE_e	ΔE_0	ΔH	ΔG
cis-CH_3SNO-Arg^+		O,N		-9.14	-8.21	-7.85	+1.80								
cis-CH_3SNO-His^+		O		-8.13	-7.29	-6.93	+2.66								
cis-CH_3SNO-His^+		N		-7.60	-6.71	-6.35	+3.47								
cis-CH_3SNO-Lys^+		O		-8.89	-7.65	-7.72	+2.46								
cis-CH_3SNO-Lys^+		N		-8.35	-7.15	-7.08	+2.34								
cis-CH_3SNO-Asp^0/Glu^0		O		-4.58	-3.79	-3.27	+4.80								
cis-CH_3SNO-Asp^0/Glu^0		N		-5.63	-4.67	-4.27	+5.11								
cis-CH_3SNO-Asp^-/Glu^-	N-S		O…S					-4.34	-3.28	-2.89	+6.70				
cis-CH_3SNO-His^0	N-S		N…S					-2.40	-2.03	-1.15	+4.53				
cis-CH_3SNO-Arg^+- Asp^-/Glu^-	N-S	O,N	O…S	-22.26	-21.30	-21.09	-10.79	-17.46	-16.37	-16.13	-5.89	-13.12	-13.09	-13.24	-12.59
cis-CH_3SNO-His^+- Asp^-/Glu^-	N-S	O	O…S	-20.70	-20.19	-19.82	-9.96	-16.91	-16.18	-15.78	-5.91	-12.57	-12.89	-12.89	-12.61
cis-CH_3SNO-Lys^+- Asp^-/Glu^-	N-S	O	O…S	-22.36	-21.63	-21.63	-11.57	-17.81	-17.26	-16.81	-7.33	-13.47	-13.98	-13.91	-14.03
cis-CH_3SNO- Asp^0/Glu^0 - Asp^-/Glu^-	N-S	O	O…S	-7.37	-6.55	-6.16	+3.20	-7.13	-6.04	-5.79	+5.10	-2.79	-2.76	-2.89	-1.60
cis-CH_3SNO- Asp^0/Glu^0- Asp^-/Glu^-	N-S	N	O…S	-7.39	-6.49	-6.15	+3.62	-6.10	-5.11	-4.77	+5.22	-1.76	-2.76	-1.88	-1.49
cis-CH_3SNO-Arg^+-His^0	N-S	O,N	N…S	-11.75	-10.04	-10.18	+3.66	-5.02	-3.85	-3.47	+6.39	-2.62	-1.82	-2.32	+1.86
cis-CH_3SNO-His^+-His^0	N-S	O	N…S	-10.72	-9.69	-9.49	+2.36	-5.00	-4.43	-3.71	+4.23	-2.60	-2.40	-2.56	-0.30
cis-CH_3SNO-His^+-His^0	N-S	N	N…S	-10.05	-8.87	-8.70	+3.66	-4.86	-4.19	-3.50	+4.73	-2.45	-2.16	-2.35	+0.19
cis-CH_3SNO-Lys^+-His^0	N-S	O	N…S	-11.80	-10.50	-10.71	+1.57	-5.32	-4.88	-4.14	+3.64	-2.92	-2.85	-2.98	-0.89
trans-CH_3SNO-Arg^+		O,N		-7.84	-6.53	-6.31	+3.70								
trans-CH_3SNO-His^+		O		-7.38	-6.79	-6.27	+2.20								
trans-CH_3SNO-His^+		N		-6.21	-5.25	-4.84	+4.59								
trans-CH_3SNO-Lys^+		O		-8.22	-7.22	-7.08	+2.06								
trans-CH_3SNO-Lys^+		N		-6.36	-4.59	-4.73	+5.50								
trans-CH_3SNO- Asp^0/Glu^0		O		-4.31	-3.53	-3.01	+5.11								
trans-CH_3SNO- Asp^0/Glu^0		N		-5.41	-4.46	-4.05	+4.75								
trans-CH_3SNO- Asp^-/Glu^-	N-S		O…S	-4.34					-3.44	-2.97	+6.05				

Complex	N-S or C-S	LA at O or N	LB···S Interaction	LA…O or N Binding energy(kcal/mol)				LB…S Binding energy(kcal/mol)				Enhancement			
				ΔE_e	ΔE_0	ΔH	ΔG	ΔE_e	ΔE_0	ΔH	ΔG	ΔE_e	ΔE_0	ΔH	ΔG
trans-CH_3SNO-His^0	N-S		N…S	-2.42					-1.92	-1.14	+5.64				
trans-CH_3SNO-Arg^+- Asp^-/Glu^-	N-S	O,N	O…S	-21.16	-19.97	-19.87	-8.75	-17.66	-16.88	-16.53	-6.39	-13.32	-13.44	-13.56	-12.45
trans-CH_3SNO-His^+- Asp^-/Glu^-	N-S	O	O…S	-19.72	-19.11	-18.88	-8.52	-16.68	-15.76	-15.58	-4.67	-12.34	-12.32	-12.61	-10.72
trans-CH_3SNO-His^+- Asp^-/Glu^-	N-S	N	O…S	-19.08	-18.20	-18.01	-7.22	-17.21	-16.36	-16.14	-5.75	-12.87	-12.95	-13.17	-11.81
trans-CH_3SNO-Lys^+- Asp^-/Glu^-	N-S	O	O…S	-21.69	-20.82	-20.95	-10.25	-17.81	-17.04	-16.84	-6.26	-13.47	-13.60	-13.87	-12.31
trans-CH_3SNO-Lys^+- Asp^-/Glu^-	N-S	N	O…S	-20.60	-19.14	-19.49	-7.35	-18.57	-17.99	-17.74	-6.80	-14.24	-14.55	-14.77	-12.86
trans-CH_3SNO- Asp^0/Glu^0 - Asp^-/Glu^-	N-S	O	O…S	-6.63	-5.46	-5.26	+5.55	-6.66	-5.36	-5.22	+6.50	-2.35	-1.93	-2.25	+0.44
trans-CH_3SNO- Asp^0/Glu^0- Asp^-/Glu^-	N-S	N	O…S	-7.09	-6.15	-5.80	+4.34	-6.02	-5.12	-4.72	+5.65	-1.69	-1.68	-1.75	-0.41
trans-CH_3SNO-Arg^+-His^0	N-S	O,N	N…S	-11.19	-9.42	-9.55	+3.61	-5.77	-4.81	-4.37	+5.55	-3.36	-2.90	-3.24	-0.09
trans-CH_3SNO-His^+-His^0	N-S	O	N…S	-10.31	-9.34	-9.15	+2.41	-5.34	-4.47	-4.01	+5.84	-2.93	-2.56	-2.88	+0.21
trans-CH_3SNO-His^+-His^0	N-S	N	N…S	-9.26	-7.95	-7.79	+4.20	-5.47	-4.61	-4.08	+5.25	-3.05	-2.70	-2.95	-0.39
trans-CH_3SNO-Lys^+-His^0	N-S	O	N…S	-11.45	-10.06	-10.26	+1.70	-5.64	-4.75	-4.32	+5.28	-3.23	-2.84	-3.18	-0.36
trans-CH_3SNO-Lys^+-His^0	N-S	N	N…S	-9.84	-7.98	-8.32	+4.63	-5.90	-5.30	-4.73	+4.77	-3.48	-3.38	-3.59	-0.87

Table S9. CH_3SNO S–N bond lengths and bond length changes upon complexation in σ-hole bound CH_3SNO complexes (in Å); PBE0- D3BJ-PCM(ε=4.2)/def2-TZVPPD calculations.

Complex	LA at O or N	N-S or C-S	*r*(S-N)	Δ*r*(S-N)
cis-CH_3SNO			1.757	
cis-CH_3SNO-Asp^-/Glu^-		N-S	1.705	-0.052
cis-CH_3SNO-His^0		N-S	1.732	-0.026
cis-CH_3SNO- Arg^+	O,N		1.675	-0.082
cis-CH_3SNO-His^+	O		1.670	-0.087
cis-CH_3SNO-His^+	N		1.701	-0.056
cis-CH_3SNO-Lys^+	O		1.666	-0.092
cis-CH_3SNO-Lys^+	N		1.698	-0.059
cis-CH_3SNO-Asp^0/Glu^0	O		1.694	-0.073
cis-CH_3SNO-Asp^0/Glu^0	N		1.714	-0.053
cis-CH_3SNO-Arg^+-Asp^-/Glu^-	O,N	N-S	1.657	-0.101
cis-CH_3SNO-His^+-Asp^-/Glu^-	O	N-S	1.644	-0.113
cis-CH_3SNO-Lys^+-Asp^-/Glu^-	O	N-S	1.644	-0.113
cis-CH_3SNO- Asp^0/Glu^0 – Asp^-/Glu^-	O	N-S	1.666	-0.101
cis-CH_3SNO- Asp^0/Glu^0 - Asp^-/Glu^-	N	N-S	1.687	-0.080
cis-CH_3SNO-Arg^+-His^0	N,O	N-S	1.667	-0.100
cis-CH_3SNO-His^+-His^0	N	N-S	1.686	-0.071
cis-CH_3SNO-His^+-His^0	O	N-S	1.658	-0.099
cis-CH_3SNO-Lys^+-His^0	O	N-S	1.653	-0.114
trans-CH_3SNO			1.767	
trans-CH_3SNO- Asp^-/Glu^-		N-S	1.727	-0.040
trans-CH_3SNO-His^0		N-S	1.746	-0.022
trans-CH_3SNO-Arg^+	N,O		1.697	-0.070
trans-CH_3SNO-His^+	O		1.694	-0.073
trans-CH_3SNO-His^+	N		1.710	-0.057
trans-CH_3SNO-Lys^+	O		1.687	-0.080
trans-CH_3SNO-Lys^+	N		1.712	-0.055
trans-CH_3SNO- Asp^0/Glu^0	O		1.718	-0.050
trans-CH_3SNO- Asp^0/Glu^0	N		1.727	-0.040
trans-CH_3SNO-Arg^+- Asp^-/Glu^-	N,O	N-S	1.681	-0.086
trans-CH_3SNO-His^+- Asp^-/Glu^-	O	N-S	1.669	-0.099
trans-CH_3SNO-His^+- Asp^-/Glu^-	N	N-S	1.694	-0.074
trans-CH_3SNO-Lys^+- Asp^-/Glu^-	O	N-S	1.665	-0.102
trans-CH_3SNO-Lys^+- Asp^-/Glu^-	N	N-S	1.695	-0.072
trans-CH_3SNO- Asp^0/Glu^0- Asp^-/Glu^-	O	N-S	1.688	-0.080
trans-CH_3SNO- Asp^0/Glu^0- Asp^-/Glu^-	N	N-S	1.702	-0.066
trans-CH_3SNO-Arg^+-His^0	N,O	N-S	1.685	-0.083
trans-CH_3SNO-His^+-His^0	O	N-S	1.679	-0.088
trans-CH_3SNO-His^+-His^0	N	N-S	1.698	-0.070
trans-CH_3SNO-Lys^+-His^0	O	N-S	1.674	-0.094
trans-CH_3SNO-Lys^+-His^0	N	N-S	1.696	-0.071

Table S10. LB–S intermolecular bond lengths in σ-hole bound CH_3SNO complexes (in Å); PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD calculations.

Complex	N-S or C-S	LA at O or N	LB···S Interaction	$r(Y\cdots S)$
cis-CH_3SNO- Asp^-/Glu^-	N-S		O···S	2.790
cis-CH_3SNO-His^0	N-S		N···S	3.252
cis-CH_3SNO-Arg^+- Asp^-/Glu^-	N-S	O,N	O···S	2.539
cis-CH_3SNO-His^+- Asp^-/Glu^-	N-S	O	O···S	2.585
cis-CH_3SNO-Lys^+- Asp^-/Glu^-	N-S	O	O···S	2.536
cis-CH_3SNO-Asp^0/Glu^0-Asp^-/Glu^-	N-S	O	O···S	2.742
cis-CH_3SNO-Asp^0/Glu^0-Asp^-/Glu^-	N-S	N	O···S	2.732
cis-CH_3SNO-Arg^+-His^0	N-S	O,N	N···S	2.837
cis-CH_3SNO-His^+-His^0	N-S	N	N···S	3.006
cis-CH_3SNO-His^+-His^0	N-S	O	N···S	2.995
cis-CH_3SNO-Lys^+-His^0	N-S	O	O···S	2.980
trans-CH_3SNO- Asp^-/Glu^-	N-S		O···S	2.783
trans-CH_3SNO-His^0	N-S		N···S	3.153
trans-CH_3SNO-Arg^+- Asp^-/Glu^-	N-S	O,N	O···S	2.446
trans-CH_3SNO-His^+- Asp^-/Glu^-	N-S	O	O···S	2.470
trans-CH_3SNO-His^+- Asp^-/Glu^-	N-S	N	O···S	2.453
trans-CH_3SNO-Lys^+- Asp^-/Glu^-	N-S	O	O···S	2.441
trans-CH_3SNO-Lys^+- Asp^-/Glu^-	N-S	N	O···S	2.426
trans-CH_3SNO-Asp^0/Glu^0-Asp^-/Glu^-	N-S	O	O···S	2.619
trans-CH_3SNO-Asp^0/Glu^0-Asp^-/Glu^-	N-S	N	O···S	2.658
trans-CH_3SNO-Arg^+-His^0	N-S	O,N	N···S	2.821
trans-CH_3SNO-His^+-His^0	N-S	O	N···S	2.857
trans-CH_3SNO-His^+-His^0	N-S	N	N···S	2.838
trans-CH_3SNO-Lys^+-His^0	N-S	O	N···S	2.980
trans-CH_3SNO-Lys^+-His^0	N-S	N	N···S	2.807

Table S11. LA–S intermolecular bond lengths in σ-hole bound CH_3SNO complexes (in Å); PBE0-D3BJ-PCM(ε=4.2)/def2-TZVPPD calculations.

Complex	N-S or C-S	LA at O or N	*r*(LA–*X*)
cis-CH_3SNO-Arg^+		O*,N	1.949
		O,N*	2.029
cis-CH_3SNO-His^+		O	1.735
cis-CH_3SNO-His^+		N	1.856
cis-CH_3SNO-Lys^+		O	1.724
cis-CH_3SNO-Lys^+		N	1.849
cis-CH_3SNO- Asp^0/Glu^0		O	1.807
cis-CH_3SNO- Asp^0/Glu^0		N	1.872
cis-CH_3SNO-Arg^+- Asp^-/Glu^-	N-S	O*,N	1.813
	N-S	O,N*	1.941
cis-CH_3SNO-His^+- Asp^-/Glu^-	N-S	O	1.628
cis-CH_3SNO-Lys^+- Asp^-/Glu^-	N-S	O	1.594
cis-CH_3SNO-Asp^0/Glu^0-Asp^-/Glu^-	N-S	O	1.704
cis-CH_3SNO-Asp^0/Glu^0-Asp^-/Glu^-	N-S	N	1.808
cis-CH_3SNO-Arg^+-His^0	N-S	O*,N	1.887
	N-S	O,N*	1.996
cis-CH_3SNO-His^+-His^0	N-S	N	1.809
cis-CH_3SNO-His^+-His^0	N-S	O	1.689
cis-CH_3SNO-Lys^+-His^0	N-S	O	1.676
trans-CH_3SNO-Arg^+		O*,N	1.946
		O,N*	2.068
trans-CH_3SNO-His^+		O	1.748
trans-CH_3SNO-His^+		N	1.937
trans-CH_3SNO-Lys^+		O	1.731
trans-CH_3SNO-Lys^+		N	1.877
trans-CH_3SNO- Asp^0/Glu^0	N-S	O	1.825
trans-CH_3SNO- Asp^0/Glu^0	N-S	N	1.925
trans-CH_3SNO-Arg^+- Asp^-/Glu^-	N-S	O*,N	1.823
	N-S	O,N*	1.933
trans-CH_3SNO-His^+- Asp^-/Glu^-	N-S	O	1.583
trans-CH_3SNO-His^+- Asp^-/Glu^-	N-S	N	1.727
trans-CH_3SNO-Lys^+- Asp^-/Glu^-	N-S	O	1.569
trans-CH_3SNO-Lys^+- Asp^-/Glu^-	N-S	N	1.710
trans-CH_3SNO-Asp^0/Glu^0-Asp^-/Glu^-	N-S	O	1.694
trans-CH_3SNO-Asp^0/Glu^0-Asp^-/Glu^-	N-S	N	1.804
trans-CH_3SNO-Arg^+-His^0	N-S	O*,N	1.877
	N-S	O,N*	2.014
trans-CH_3SNO-His^+-His^0	N-S	O	1.685
trans-CH_3SNO-His^+-His^0	N-S	N	1.835
trans-CH_3SNO-Lys^+-His^0	N-S	O	1.664
trans-CH_3SNO-Lys^+-His^0	N-S	N	1.813