Supplementary Material

High-accuracy theoretical thermochemistry of atmospherically important sulfur-containing molecules

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Table 1: Contributions to the total energies for the species studied in this work. All values are in atomic units.

Species	E_{HF}[a]	$\Delta E_{CCSD(T)}$[b]	$\Delta E_{CCSDT(Q)}$[c]	ΔE_{core}[d]	ΔE_{ZPE}[e]	ΔE_{DBOC}[f]	ΔE_{REL}[g]	Total
HSO	-472.992011	-0.489026	-0.002240	-0.493830	0.010312	0.008578	-1.166381	-475.124597
HOS	-472.994366	-0.483176	-0.001766	-0.493784	0.013127	0.008553	-1.166620	-475.118032
$HOSO_2$	-622.776220	-1.049757	-0.002731[h]	-0.620804	0.022254	0.013297	-1.275932	-625.690012
trans-HSNO	-527.403071	-0.739828	-0.004347	-0.553842	0.014798	0.010583	-1.197979	-529.873686
cis-HSNO	-527.402186	-0.739293	-0.004200	-0.553854	0.014586	0.010582	-1.198000	-529.872366
SH	-398.110827	-0.204179	-0.001046	-0.430225	0.006080	0.006099	-1.112194	-399.846291
CH_2SO	-511.440346	-0.703443	-0.003053	-0.551792	0.028665	0.010436	-1.182216	-513.841750
CH_2SH	-437.140131	-0.417342	-0.001793	-0.488212	0.032582	0.008288	-1.126960	-439.133634
SCSOH	-908.394168	-0.886398	-0.004208[h]	-0.981995	0.019413	0.015970	-2.293658	-912.525083
S_2COH	-908.437105	-0.879630	0.012033[h]	-0.981912	0.021882	0.015968	-2.293870	-912.542634
C	-37.693785	-0.095914	-0.000497	-0.055802	0.000000	0.001710	-0.016425	-37.860713
S	-397.513315	-0.162177	-0.000923	-0.429887	0.000000	0.005813	-1.112536	-399.213024
H_2	-1.133661	-0.040912	0.000000	0.000000	0.009929	0.000522	-0.000013	-1.164135
O_2	-149.691988	-0.510187	-0.001789	-0.126490	0.003643	0.004874	-0.110954	-150.432893
N_2	-108.993235	-0.429838	-0.001512	-0.120889	0.005380	0.004127	-0.062717	-109.598684

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Table 1 – Continued

Species	E_{HF}[a]	$\Delta E_{CCSD(T)}$[b]	$\Delta E_{CCSDT(Q)}$[c]	ΔE_{core}[d]	ΔE_{ZPE}[e]	ΔE_{DBOC}[f]	ΔE_{REL}[g]	Total

[a] E_{HF} was obtained by extrapolating aug-cc-pV(X+d)Z (X=T,Q,5) energies.

[b] $\Delta E_{CCSD(T)}$ is the valence correlation energy calculated by the CCSD(T) method and extrapolated to the basis set limit using aug-cc-pV(X+d)Z (X = Q,5) results.

[c] Unless otherwise noted, $\Delta E_{CCSDT(Q)}$ is obtained by subtracting $E_{CCSD(T)}$ from $E_{CCSDT(Q)}$ calculated with the cc-pV(T+d)Z basis set.

[d] ΔE_{core} is the core-correlation energy defined as the extrapolated difference between the frozen-core and all-electron CCSD(T) energies. The cc-pCVTZ and the cc-pCVQZ basis sets were used.

[e] ΔE_{ZPE} values were determined from all-electron CCSD(T) calculations. For harmonic frequencies and anharmonic contributions the cc-pVQZ and cc-pVTZ basis sets were used, respectively.

[f] ΔE_{DBOC} was calculated at the CCSD/cc-pCVTZ level.

[g] ΔE_{REL} was obtained at the CCSD(T)/cc-pCVTZ level, and it includes the spin-orbit corrections for S and C atoms as well as for SH, which are -892, -135, and -859 μE_h, respectively.

[h] $\Delta E_{CCSDT(Q)}$ was estimated using a reduced virtual space (see text).

Table 2: Calculated bond lengths (in Å), bond angles, dihedral angles (in degrees), rotational constants (in GHz), harmonic vibrational frequencies (in cm^{-1}), anharmonicity constants (in cm^{-1}), and G_0 terms (in cm^{-1}) for the species studied in this work.

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
HSO	R(SO)= 1.50169	⟨(OSH)= 104.46		19.091	$\omega_1 = 1029$	$x_{11} = -6.4$	-4.4
	R(SH)= 1.36721			20.383	$\omega_2 = 1103$	$x_{12} = -14.2$	
				301.253	$\omega_3 = 2450$	$x_{13} = 2.3$	
						$x_{22} = -3.9$	
						$x_{23} = -13.4$	
						$x_{33} = -58.6$	
SOH	R(SO)= 1.63627	⟨(SOH)= 107.82		16.164	$\omega_1 = 858$	$x_{11} = -4.8$	-10.1
	R(OH)= 0.96193			16.575	$\omega_2 = 1193$	$x_{12} = -5.7$	
				652.125	$\omega_3 = 3798$	$x_{13} = -1.5$	
						$x_{22} = -9.8$	
						$x_{23} = -21.1$	
						$x_{33} = -89.6$	
$HOSO_2$[a]	$R(SO_1)$= 1.61371	⟨(HO_1S)= 107.34	$D(O_2SO_1H)$= 26.09	4.898	$\omega_1 = 301$	$x_{11} = 1.5$	-4.5
	$R(SO_2)$= 1.44671	⟨(O_1SO_2)= 107.95	$D(O_3SO_1H)$= 159.84	9.039	$\omega_2 = 432$	$x_{12} = -12.1$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
	$R(SO_3)$= 1.43848	$\langle(O_1SO_3)$= 105.77		9.380	$\omega_3 = 435$	$x_{13} = -5.7$	
	$R(HO_1)$= 0.96582	$\langle(O_2SO_3)$= 123.33			$\omega_4 = 539$	$x_{14} = -3.7$	
					$\omega_5 = 794$	$x_{15} = -4.4$	
					$\omega_6 = 1122$	$x_{16} = -0.7$	
					$\omega_7 = 1136$	$x_{17} = 6.8$	
					$\omega_8 = 1347$	$x_{18} = -4.5$	
					$\omega_9 = 3783$	$x_{19} = -6.7$	
						$x_{22} = -1.3$	
						$x_{23} = -1.1$	
						$x_{24} = -1.2$	
						$x_{25} = -4.4$	
						$x_{26} = -0.8$	
						$x_{27} = 0.4$	
						$x_{28} = -1.6$	
						$x_{29} = -2.6$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{33} = -0.1$	
						$x_{34} = -0.8$	
						$x_{35} = -2.7$	
						$x_{36} = -2.8$	
						$x_{37} = 0.1$	
						$x_{38} = -3.5$	
						$x_{39} = -0.4$	
						$x_{44} = -0.4$	
						$x_{45} = -2.5$	
						$x_{46} = -2.7$	
						$x_{47} = 1.7$	
						$x_{48} = -4.0$	
						$x_{49} = -0.3$	
						$x_{55} = -5.7$	
						$x_{56} = -1.5$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{57} = -5.2$	
						$x_{58} = -0.2$	
						$x_{59} = -0.9$	
						$x_{66} = -4.1$	
						$x_{67} = -1.5$	
						$x_{68} = -14.6$	
						$x_{69} = -0.9$	
						$x_{77} = -7.9$	
						$x_{78} = -6.4$	
						$x_{79} = -21.9$	
						$x_{88} = -6.0$	
						$x_{89} = -2.5$	
						$x_{99} = -82.4$	
trans-HSNO	R(SH)= 1.33693	$\langle$(HSN)= 90.33	D(ONSH)= 180.00	5.739	$\omega_1 = 320$	$x_{11} = 0.3$	-3.8
	R(SN)= 1.85183	$\langle$(ONS)= 114.53		6.244	$\omega_2 = 391$	$x_{12} = -2.6$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
	R(NO)= 1.17645			70.926	$\omega_3 = 574$	$x_{13} = -3.4$	
					$\omega_4 = 919$	$x_{14} = -5.2$	
					$\omega_5 = 1642$	$x_{15} = 6.6$	
					$\omega_6 = 2716$	$x_{16} = -1.4$	
						$x_{22} = -6.8$	
						$x_{23} = -2.0$	
						$x_{24} = -4.1$	
						$x_{25} = 4.2$	
						$x_{26} = -5.8$	
						$x_{33} = -4.0$	
						$x_{34} = -14.5$	
						$x_{35} = 7.0$	
						$x_{36} = -3.4$	
						$x_{44} = -4.6$	
						$x_{45} = 4.5$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{46} = -14.7$	
						$x_{55} = -18.2$	
						$x_{56} = -0.9$	
						$x_{66} = -48.1$	
cis-HSNO	R(SH)= 1.34355	$\langle$(HSN)= 95.11	D(ONSH)= 0.00	5.834	$\omega_1 = 337$	$x_{11} = -0.5$	-5.3
	R(SN)= 1.83490	$\langle$(ONS)= 115.83		6.384	$\omega_2 = 420$	$x_{12} = -6.9$	
	R(NO)= 1.18029			67.784	$\omega_3 = 528$	$x_{13} = -6.4$	
					$\omega_4 = 899$	$x_{14} = -7.1$	
					$\omega_5 = 1620$	$x_{15} = 11.3$	
					$\omega_6 = 2661$	$x_{16} = -0.3$	
						$x_{22} = -10.4$	
						$x_{23} = 1.3$	
						$x_{24} = -2.4$	
						$x_{25} = 7.1$	
						$x_{26} = 0.7$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{33} = -1.6$	
						$x_{34} = -3.9$	
						$x_{35} = 3.8$	
						$x_{36} = -5.5$	
						$x_{44} = -4.8$	
						$x_{45} = 5.1$	
						$x_{46} = -12.6$	
						$x_{55} = -18.2$	
						$x_{56} = -2.0$	
						$x_{66} = -49.3$	
SH	R(SH)= 1.34175			287.322	$\omega_1 = 2690$	$x_{11} = -48.3$	1.5
				287.322			
CH_2SO[b]	R(SO)= 1.47336	$\langle$(CSO)= 114.69	D(H_1CSO)= 0.00	7.596	$\omega_1 = 390$	$x_{11} = 0.7$	25.3
	R(SC)= 1.61317	$\langle$(H_1CS)= 122.96	D(H_2CSO)= 180.00	9.374	$\omega_2 = 642$	$x_{12} = 0.3$	
	R(H_1C)= 1.07911	$\langle$(H_2CS)= 115.48		40.058	$\omega_3 = 780$	$x_{13} = 0.5$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
	$R(H_2C)$= 1.07921				$\omega_4 = 879$	$x_{14} = -0.5$	
					$\omega_5 = 997$	$x_{15} = -1.8$	
					$\omega_6 = 1193$	$x_{16} = -2.7$	
					$\omega_7 = 1416$	$x_{17} = -0.3$	
					$\omega_8 = 3160$	$x_{18} = -1.5$	
					$\omega_9 = 3287$	$x_{19} = -1.8$	
						$x_{22} = -2.5$	
						$x_{23} = 72.6$	
						$x_{24} = 0.5$	
						$x_{25} = -3.9$	
						$x_{26} = -3.2$	
						$x_{27} = -72.1$	
						$x_{28} = -5.3$	
						$x_{29} = -4.3$	
						$x_{33} = 4.3$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{34} = 2.0$	
						$x_{35} = -2.9$	
						$x_{36} = 0.2$	
						$x_{37} = -106.6$	
						$x_{38} = -10.6$	
						$x_{39} = -18.0$	
						$x_{44} = -1.5$	
						$x_{45} = -2.6$	
						$x_{46} = -3.1$	
						$x_{47} = -8.7$	
						$x_{48} = -7.7$	
						$x_{49} = -9.0$	
						$x_{55} = -3.6$	
						$x_{56} = -3.5$	
						$x_{57} = -5.5$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{58} = -3.4$	
						$x_{59} = -3.2$	
						$x_{66} = -6.1$	
						$x_{67} = -1.2$	
						$x_{68} = -1.0$	
						$x_{69} = -1.1$	
						$x_{77} = -8.7$	
						$x_{78} = -5.8$	
						$x_{79} = -21.0$	
						$x_{88} = -27.8$	
						$x_{89} = -112.5$	
						$x_{99} = -30.9$	
CH_2SH[c]	$R(H_1S) = 1.33711$	$\langle(H_1SC) = 97.63$	$D(H_1SCH_2) = 0.00$	14.121	$\omega_1 = 94$	$x_{11} = 625.5$	157.9
	$R(SC) = 1.71659$	$\langle(H_2CS) = 121.56$	$D(H_1SCH_3) = 180.00$	15.638	$\omega_2 = 347$	$x_{12} = 324.4$	
	$R(H_2S) = 1.07343$	$\langle(H_3CS) = 116.98$		145.632	$\omega_3 = 785$	$x_{13} = 14.4$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
	$R(H_3S)$= 1.07439	$\langle(H_2CH_3)$= 121.46			$\omega_4 = 857$	$x_{14} = -20.4$	
					$\omega_5 = 1076$	$x_{15} = 15.0$	
					$\omega_6 = 1425$	$x_{16} = 1.0$	
					$\omega_7 = 2709$	$x_{17} = -25.2$	
					$\omega_8 = 3202$	$x_{18} = -79.1$	
					$\omega_9 = 3331$	$x_{19} = -86.9$	
						$x_{22} = 18.7$	
						$x_{23} = -0.2$	
						$x_{24} = -37.8$	
						$x_{25} = -0.4$	
						$x_{26} = 1.2$	
						$x_{27} = -11.4$	
						$x_{28} = -57.0$	
						$x_{29} = -32.0$	
						$x_{33} = 0.5$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{34} = -0.9$	
						$x_{35} = -5.5$	
						$x_{36} = -5.0$	
						$x_{37} = -4.8$	
						$x_{38} = -4.1$	
						$x_{39} = -4.5$	
						$x_{44} = -3.7$	
						$x_{45} = -4.9$	
						$x_{46} = -4.7$	
						$x_{47} = -1.5$	
						$x_{48} = -0.8$	
						$x_{49} = -0.3$	
						$x_{55} = -1.7$	
						$x_{56} = -5.2$	
						$x_{57} = -13.2$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{58} = -4.9$	
						$x_{59} = -5.2$	
						$x_{66} = -7.5$	
						$x_{67} = -1.2$	
						$x_{68} = -5.4$	
						$x_{69} = -20.9$	
						$x_{77} = -48.8$	
						$x_{78} = -0.3$	
						$x_{79} = -0.3$	
						$x_{88} = -28.3$	
						$x_{89} = -113.5$	
						$x_{99} = -31.9$	
S_2COH[d]	$R(S_1C) = 1.66583$	$\langle(S_1CS_2) = 111.49$	$D(S_1COH) = 0.00$	2.605	$\omega_1 = 275$	$x_{11} = -1.0$	-12.9
	$R(S_2C) = 1.66476$	$\langle(S_1CO) = 126.16$	$D(S_2COH) = 180.00$	4.145	$\omega_2 = 398$	$x_{12} = -0.3$	
	$R(CO) = 1.32276$	$\langle(S_2CO) = 122.35$		7.015	$\omega_3 = 501$	$x_{13} = 2.3$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
	R(OH)= 0.96619	$\langle$(COH)= 107.90			$\omega_4 = 567$	$x_{14} = 1.7$	
					$\omega_5 = 686$	$x_{15} = -1.7$	
					$\omega_6 = 901$	$x_{16} = -3.6$	
					$\omega_7 = 1298$	$x_{17} = -1.2$	
					$\omega_8 = 1363$	$x_{18} = -1.6$	
					$\omega_9 = 3747$	$x_{19} = -2.1$	
						$x_{22} = 0.0$	
						$x_{23} = 0.4$	
						$x_{24} = -0.4$	
						$x_{25} = 0.3$	
						$x_{26} = -3.0$	
						$x_{27} = 0.7$	
						$x_{28} = -4.0$	
						$x_{29} = -1.6$	
						$x_{33} = -0.8$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{34} = -9.4$	
						$x_{35} = -1.7$	
						$x_{36} = -4.5$	
						$x_{37} = -2.1$	
						$x_{38} = -3.8$	
						$x_{39} = -1.2$	
						$x_{44} = -12.9$	
						$x_{45} = -0.8$	
						$x_{46} = -2.9$	
						$x_{47} = 8.7$	
						$x_{48} = 6.9$	
						$x_{49} = -0.9$	
						$x_{55} = -3.1$	
						$x_{56} = -6.7$	
						$x_{57} = -2.5$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{58} = 4.4$	
						$x_{59} = -0.8$	
						$x_{66} = -3.2$	
						$x_{67} = -5.0$	
						$x_{68} = -6.7$	
						$x_{69} = -1.3$	
						$x_{77} = -9.3$	
						$x_{78} = -16.1$	
						$x_{79} = -10.5$	
						$x_{88} = -7.8$	
						$x_{89} = -14.6$	
						$x_{99} = -88.3$	
SCSOH[e]	$R(S_1C) = 1.57014$	$\langle(S_1CS_2) = 163.27$	$D(OS_2CS_1) = -2.93$	2.023	$\omega_1 = 102$	$x_{11} = 0.0$	-9.7
	$R(S_2C) = 1.59514$	$\langle(CS_2O) = 110.58$	$D(HOS_2C) = 77.22$	2.291	$\omega_2 = 216$	$x_{12} = 0.1$	
	$R(S_2O) = 1.70201$	$\langle(S_2OH) = 107.21$		16.488	$\omega_3 = 384$	$x_{13} = 0.7$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
	R(OH)= 0.96304				$\omega_4 = 399$	$x_{14} = -2.2$	
					$\omega_5 = 612$	$x_{15} = 6.0$	
					$\omega_6 = 620$	$x_{16} = 3.1$	
					$\omega_7 = 1104$	$x_{17} = 2.8$	
					$\omega_8 = 1412$	$x_{18} = -8.8$	
					$\omega_9 = 3798$	$x_{19} = 0.1$	
						$x_{22} = -14.6$	
						$x_{23} = -2.8$	
						$x_{24} = -16.0$	
						$x_{25} = -4.4$	
						$x_{26} = 0.4$	
						$x_{27} = 3.0$	
						$x_{28} = 3.7$	
						$x_{29} = -4.9$	
						$x_{33} = -4.0$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{34} = 1.0$	
						$x_{35} = -11.0$	
						$x_{36} = -2.1$	
						$x_{37} = -2.5$	
						$x_{38} = 5.4$	
						$x_{39} = -1.0$	
						$x_{44} = 0.1$	
						$x_{45} = -0.7$	
						$x_{46} = -6.6$	
						$x_{47} = 0.6$	
						$x_{48} = -6.6$	
						$x_{49} = -0.5$	
						$x_{55} = -13.4$	
						$x_{56} = -0.3$	
						$x_{57} = -14.4$	

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Table 2 – Continued

Species	Bond lengths	Bond angles	Dihedral angles	Rotational constants	Harmonic vibrational frequencies	Anharmonicity constants	G_0
						$x_{58} = 12.9$	
						$x_{59} = -2.5$	
						$x_{66} = -1.5$	
						$x_{67} = 1.1$	
						$x_{68} = -5.8$	
						$x_{69} = 0.0$	
						$x_{77} = -10.0$	
						$x_{78} = 4.0$	
						$x_{79} = -21.8$	
						$x_{88} = -14.1$	
						$x_{89} = 0.6$	
						$x_{99} = -85.7$	

[a] O_1: the oxygen atom to which the hydrogen is attached, O_2: *cis* position relative to the H atom, O_3: *trans* position relative to the H atom

[b] H_1: *cis* position relative to the O atom, H_2: *trans* position relative to the O atom

[c] H_1: the H atom connected to sulfur, H_2: *cis* position relative to H_1, H_3: *trans* position relative to H_1

[d] S_1: *cis* position relative to the H atom, S_2: *trans* position relative to the H atom

[e] S_2: this sulfur atom is connected to the O atom