Supplementary Material

Sulfur as a hydrogen bond donor in the gas phase: Rotational spectroscopic and computational study of 3-mercaptopropionic acid

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Appendix I Equilibrium geometries of the most stable conformers of 3-mpa, 3-hydroxypropionic acid, and thioglycolic acid obtained at the B3LYP-D3BJ/aug-cc-pVTZ

Table S1 Cartesian coordinates for the equilibrium structure of **mpa1.**

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
S	2.025950	-0.374449	-0.378647
C	1.011011	0.802535	0.594268
C	-0.361543	1.079127	0.003449
C	-1.295690	-0.100470	0.090157
O	-1.099011	-1.113255	0.712507
O	-2.430520	0.112568	-0.613735
H	-2.989660	-0.670282	-0.500411
H	1.300551	-1.467592	-0.085709
H	1.593455	1.721289	0.614029
H	0.928960	0.433910	1.613349
H	-0.290249	1.388985	-1.039027
H	-0.844668	1.903211	0.538708

Table S2 Cartesian coordinates for the equilibrium structure of **mpa2.**

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
S	-2.555543	-0.110900	-0.085537
C	-0.857051	0.551824	0.083597
C	0.216311	-0.518110	-0.032697
C	1.609540	0.059294	-0.007454
O	1.888186	1.230507	0.003776
O	2.549585	-0.915301	-0.007205
H	3.414325	-0.478692	-0.003886
H	-2.550497	-0.868518	1.026529
H	-0.769788	1.097187	1.019436
H	-0.758719	1.279034	-0.719301
H	0.102149	-1.083393	-0.959545
H	0.136246	-1.250921	0.772108

Table S3 Cartesian coordinates for the equilibrium structure of **mpa3.**

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
S	-1.953816	-0.527169	0.301249
C	-1.017892	0.761003	-0.610379
C	0.329150	1.089294	0.013523
C	1.312831	-0.049083	-0.110618
O	1.324795	-0.865101	-0.994585
O	2.231600	-0.030554	0.881684
H	2.844425	-0.762548	0.716304
H	-2.278505	0.236575	1.360456
H	-1.632799	1.652999	-0.695031
H	-0.877709	0.348405	-1.606639
H	0.232105	1.374440	1.059444
H	0.777846	1.942794	-0.506468

Table S4 Cartesian coordinates for the equilibrium structure of **mpa4.**

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
S	-2.502745	-0.238364	-0.000058
C	-0.854837	0.575107	0.000255
C	0.209908	-0.508663	-0.000160
C	1.604075	0.063779	-0.000048
O	1.887838	1.233572	-0.000158
O	2.538313	-0.915620	0.000161
H	3.405485	-0.484070	0.000150
H	-3.235637	0.888482	0.000300
H	-0.757610	1.201621	0.882393
H	-0.757599	1.202296	-0.881398
H	0.112634	-1.160068	0.871100
H	0.112573	-1.159398	-0.871923

Table S5 Cartesian coordinates for the equilibrium structure of **mpa5.**

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
S	-2.531061	0.046734	0.033228
C	0.206699	-0.360283	0.528740
C	-0.782322	0.243829	-0.470866
C	1.634174	-0.153172	0.086301
O	2.393578	-1.015893	-0.269804
O	1.981129	1.158012	0.112985
H	0.046585	-1.430931	0.627465
H	0.063756	0.105855	1.503456
H	-0.635314	1.318711	-0.549649
H	-0.645925	-0.184109	-1.461785
H	-2.577504	-1.294430	-0.063657
H	2.896424	1.217968	-0.197970

Table S6 Cartesian coordinates for the equilibrium structure of **mpa6.**

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
S	1.871609	-0.626358	0.006631
C	0.995022	0.960338	-0.271123
C	-0.334193	1.068790	0.467570
C	-1.330287	-0.011062	0.122069
O	-1.993694	-0.625444	0.914341
O	-1.432330	-0.195828	-1.216436
H	-2.083742	-0.898181	-1.357116
H	2.062838	-0.473877	1.329785
H	1.647898	1.784295	0.006684
H	0.841788	1.002253	-1.346690
H	-0.798831	2.029150	0.221669
H	-0.190760	1.039869	1.545227

Table S7 Cartesian coordinates for the equilibrium structure of **mpa7.**

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
S	-1.187646	-1.506191	-0.113572
C	-0.999156	0.766732	0.622556
C	0.349331	1.152159	0.027625
C	1.363024	0.039285	-0.077513
O	-1.636458	1.647595	0.672615
O	-0.892607	0.376393	1.630417
H	0.809052	1.923819	0.655100
H	0.236003	1.572354	-0.968907
H	2.214254	-0.042773	-0.922142
H	1.246468	-0.869186	0.925211
H	1.952822	-1.519471	0.797774
H	-1.952884	-0.434242	-0.383374

Table S8 Cartesian coordinates for the equilibrium structure of 3-hydroxypropionic acid.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
H	1.420675	1.292464	-0.324472
O	2.012055	0.538396	-0.439732
C	1.509971	-0.504598	0.376907
C	0.132712	-0.985044	-0.066889
C	-0.911051	0.094269	0.036295
H	2.219042	-1.327565	0.299043
H	1.471343	-0.194475	1.426393
H	-0.194748	-1.844538	0.521671
H	0.163524	-1.313994	-1.108629
O	-0.692408	1.259762	0.270855
O	-2.157768	-0.375339	-0.177751
H	-2.764674	0.377798	-0.118852

Table S9 Cartesian coordinates for the equilibrium structure of thioglycolic acid.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.309027	-0.120512	0.874939
H	-0.323487	-1.109025	1.324345
H	-0.424679	0.640924	1.639470
S	-1.741214	-0.076395	-0.273290
H	-1.586044	1.208988	-0.639161
C	0.971985	0.116242	0.121108
O	1.421153	1.202547	-0.139144
O	1.562357	-1.038501	-0.255361
H	2.347801	-0.805308	-0.772252

Appendix II Rotational parameters and relative energies for the conformers of 3-mpa calculated at B3LYP, ωB97X-D, and M062-X methods with the aug-cc-pVTZ

Table S10 Rotational parameters and relative energies for the most stable conformers of 3-mercaptopropionic acid calculated at different DFT methods (B3LYP, ωB97X-D, M062-X) with the aug-cc-pVTZ basis set.

	B3LYP			ωB97X-D			M062-X		
Conformer	**A/B/C[a]**	**$\|\mu_a\|/\|\mu_b\|/\|\mu_c\|$[b]**	**ΔE_{ZPE}[c]/ΔG[d]**	**A/B/C**	**$\|\mu_a\|/\|\mu_b\|/\|\mu_c\|$**	**$\Delta E_{ZPE}/\Delta G$**	**A/B/C**	**$\|\mu_a\|/\|\mu_b\|/\|\mu_c\|$**	**$\Delta E_{ZPE}/\Delta G$**
mpa1	5972/1544/1415	1.6/1.6/0.1	0.0/1.7	6001/1571/1437	1.7/1.6/0.1	0.0/0.0	5999/1601/1457	1.6/1.6/0.1	0.0/0.0
mpa2	9028/1158/1045	1.0/1.4/0.6	1.2/0.0	9105/1172/1057	1.1/1.5/0.7	2.5/0.4	9118/1177/1062	1.0/1.4/0.6	5.9/6.3
mpa3	5494/1523/1481	0.7/2.5/0.7	3.8/3.4	5486/1554/1512	0.7/2.5/0.9	4.6/3.3	5560/1594/1523	0.7/2.5/0.7	6.7/7.1
mpa4	8970/1178/1054	0.6/0.4/0.0	3.8/2.1	9058/1190/1066	0.7/0.4/0.0	5.4/3.3	9065/1197/1072	0.6/0.3/0.0	7.1/5.4
mpa5	8399/1173/1085	0.2/0.8/0.0	5.9/3.4	8520/1188/1096	0.2/0.8/0.0	7.5/4.6	8587/1196/1098	0.1/0.8/0.0	11.3/10.9
mpa6	4988/1610/1588	0.4/2.0/0.9	7.1/6.7	4967/1659/1627	0.4/2.1/0.8	7.5/6.3	4876/1724/1679	0.4/2.1/0.7	9.2/10.0
mpa7	5303/1578/1518	0.0/0.4/2.2	7.1/6.3	5296/1618/1555	0.0/0.4/2.2	7.1/6.7	5212/1667/1598	0.0/0.5/2.2	9.2/10.0

[a]Rotational constants (A, B, and C) in MHz; [b]Absolute values of the electric dipole moment components in D; [c]Relative energies, in kJ mol^{-1}, with respect to the global energy minimum accounting for zero-point energy (ZPE) corrections; [d]Relative Gibbs free energies, in kJ mol^{-1}, with respect to the global energy minimum calculated at 298K.

Appendix III Assigned rotational transitions for the parent species of conformer **mpa1**

Table S11 Observed frequencies and residuals for the rotational transitions of the parent species of conformer **mpa1**.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs} /MHz	$\nu_{obs-calc}$/MHz
4	0	4	3	1	3	8067.81215	-0.00022
3	1	3	2	1	2	8891.62818	0.00032
3	0	3	2	0	2	9086.37917	0.00021
3	2	2	2	2	1	9099.21433	0.00071
3	2	1	2	2	0	9111.90939	-0.00040
3	1	2	2	1	1	9302.62284	-0.00048
2	1	2	1	0	1	10290.18946	-0.00033
5	0	5	4	1	4	11317.84449	-0.00112
8	2	6	8	1	7	11545.58994	0.00022
7	2	5	7	1	6	11809.26445	-0.00034
4	1	4	3	1	3	11851.81687	0.00057
6	2	4	6	1	5	12096.13033	-0.00014
4	0	4	3	0	3	12100.34691	0.00013
4	2	3	3	2	2	12129.73237	-0.00049
4	3	2	3	3	1	12138.64209	0.00166
4	3	1	3	3	0	12138.91674	0.00024
4	2	2	3	2	1	12161.39873	0.00006
5	2	3	5	1	4	12385.20966	0.00025
4	1	3	3	1	2	12399.60213	-0.00049
4	2	2	4	1	3	12657.22379	-0.00027
3	2	1	3	1	2	12895.42816	0.00015
2	2	0	2	1	1	13086.14157	0.00004
3	1	3	2	0	2	13118.91291	-0.00045
2	2	1	2	1	2	13494.00104	-0.00055
3	2	2	3	1	3	13701.58708	-0.00027
4	2	3	4	1	4	13979.50432	0.00040
5	2	4	5	1	5	14328.59102	0.00051
6	0	6	5	1	5	14597.16279	-0.00018
5	1	5	4	1	4	14808.97990	0.00057
5	0	5	4	0	4	15101.85039	0.00085
5	2	4	4	2	3	15158.06557	-0.00034
5	3	3	4	3	2	15175.84054	-0.00080
5	3	2	4	3	1	15176.80742	0.00056
5	2	3	4	2	2	15221.08815	-0.00036
5	1	4	4	1	3	15493.10315	-0.00001
4	1	4	3	0	3	15884.35082	0.00012
6	1	6	5	1	5	17762.52626	0.00035
7	0	7	6	1	6	17892.38338	0.00036
6	0	6	5	0	5	18088.29715	0.00046
6	2	5	5	2	4	18183.66902	-0.00034
6	3	4	5	3	3	18214.49154	-0.00018
6	3	3	5	3	2	18217.06209	-0.00096
6	2	4	5	2	3	18292.99983	0.00034
6	1	5	5	1	4	18582.07862	0.00019
5	1	5	4	0	4	18592.98272	-0.00053