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

Supporting information for:

Expanding the range of binding energies and oxidizability of biologically relevant S-aromatic interactions: Imidazolium and phenolate binding to sulfoxide and sulfone

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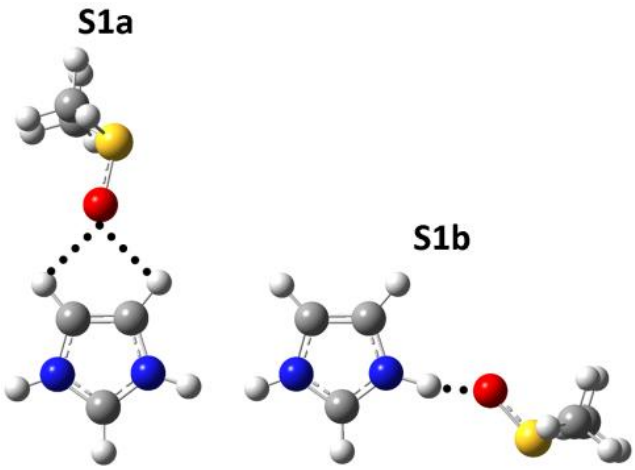

Fig. S1. Optimized geometries of the Me_2SO-imidazolium conformers at the MP2(full)/6-311++G(d,p) level of theory in the gas phase. Atom color code: hydrogen (white), carbon (gray), nitrogen (blue), oxygen (red) and sulfur (yellow). Dotted black lines show intermolecular σ-type H-bonds. The atomic coordinates are provided starting on page S11. The global minimum conformer **1a** is shown in Fig. 2 of the main text but not here.

Table S1. Ab initio equilibrium distance (r_{SX}, Å), angle (θ_{SXY}, degrees), binding energy (E and E^{CP}, kcal/mol), net charge of Me_2SO in the cationic complexes (e), IPV (eV), sum of Mulliken atomic spin densities for Me_2SO in the (+2) radicals, and the MM binding energy (kcal/mol) calculated with the default (E^{MM}) and optimized ($E^{MM,\,opt}$) FF for the Me_2SO-imidazolium conformers in Fig. S1

Conformer	r_{SX}	θ_{SXY}	E	E^{CP}	E^{MM}	$E^{MM,opt}$	*Me_2SO charge*	*Me_2SO spin density*	*IPV* [a]
S1a	5.174	90	−20.02	−17.77	−19.64	−20.34	0.02	1.0	12.21
S1b	5.018	90	−35.54	−30.77	−24.50	−31.48	0.10	1.0	13.24
1a [b]	4.988	90	−35.96	−31.13	−24.49	−31.42	0.10	1.0	13.26

[a] The IPV of free Me_2SO is 9.20 eV (see Footnote c to Table 2 of the main text).

[b] The structure of the global minimum conformer **1a** is shown in Fig. 2 of the main text.

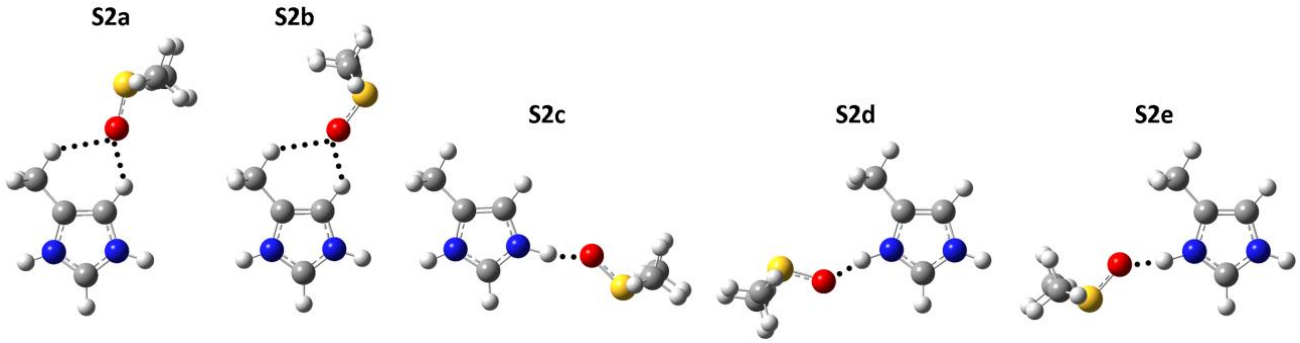

Fig. S2. Optimized geometries of the Me_2SO-4-methylimidazolium conformers at the MP2(full)/6-311++G(d,p) level of theory in the gas phase. See Fig. S1 for details of the structure representation and the atomic coordinates are provided starting on page S11. The global minimum conformer **1b** is shown in Fig. 2 of the main text but not here.

Table S2. Ab initio equilibrium distance (r_{SX}, Å), angle (θ_{SXY}, degrees), binding energy (E and E^{CP}, kcal/mol), net charge of Me_2SO in the cationic complexes (e), IPV (eV), sum of Mulliken atomic spin densities for Me_2SO in the (+2) radicals, and the MM binding energy (kcal/mol) calculated with the default (E^{MM}) and optimized ($E^{MM,\,opt}$) FF for the Me_2SO-4-methylimidazolium conformers in Fig. S2

Conformer	r_{SX}	θ_{SXY}	E	E^{CP}	E^{MM}	$E^{MM,opt}$	Me_2SO charge	Me_2SO spin density	IPV[a]
S2a	5.482	90	−20.09	−17.45	−17.12	−17.59	0.02	1.0	12.20
S2b	5.431	90	−20.66	−17.69	−17.09	−17.58	0.03	1.0	12.21
S2c	5.033	90	−33.97	−29.23	−24.19	−31.11	0.09	1.0	13.10
S2d	4.996	90	−34.29	−29.23	−24.29	−31.20	0.10	1.0	13.15
S2e	5.025	90	−34.25	−29.34	−24.28	−31.17	0.10	1.0	13.15
1b [b]	5.004	90	−34.32	−29.52	−24.16	−31.02	0.10	1.0	13.13

[a] The IPV of free Me_2SO is 9.20 eV (see Footnote c to Table 2 of the main text).

[b] The structure of the global minimum conformer **1b** is shown in Fig. 2 of the main text.

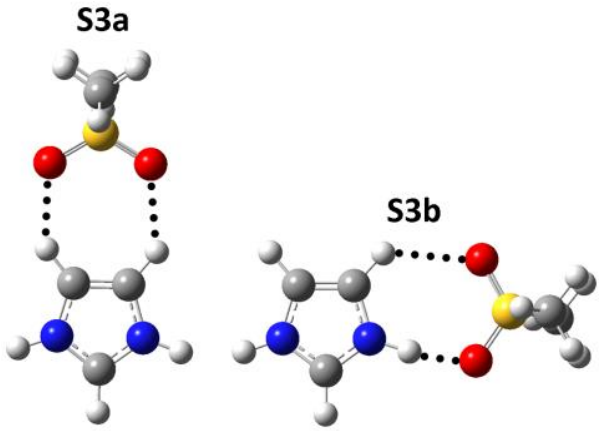

Fig. S3. Optimized geometries of the Me_2SO_2-imidazolium conformers at the MP2(full)/6-311++G(d,p) level of theory in the gas phase. See Fig. S1 for details of the structure representation and the atomic coordinates are provided starting on page S11. The global minimum conformer **2a** is shown in Fig. 2 of the main text but not here.

Table S3. Ab initio equilibrium distance (r_{SX}, Å), angle (θ_{SXY}, degrees), binding energy (E and E^{CP}, kcal/mol), net charge of Me_2SO_2 in the cationic complexes (e), IPV (eV), sum of Mulliken atomic spin densities for Me_2SO_2 in the (+2) radicals, and the MM binding energy calculated with the default FF (E^{MM}, kcal/mol) for the Me_2SO_2-imidazolium conformers in Fig. S3

Conformer	r_{SX}	θ_{SXY}	E	E^{CP}	E^{MM}	Me_2SO_2 charge	Me_2SO_2 spin density	IPV[a]
S3d	4.715	90	−19.78	−17.16	−20.46	0.02	0.0	14.26
S3e	4.574	90	−29.00	−25.03	−24.63	0.07	0.0	14.11
2a [b]	4.547	90	−29.55	−25.62	−26.07	0.06	0.0	14.12

[a] The IPV of free imidazolium is 15.34 eV (see Footnote c to Table 2 of the main text).

[b] The structure of the global minimum conformer **2a** is shown in Fig. 2 of the main text.

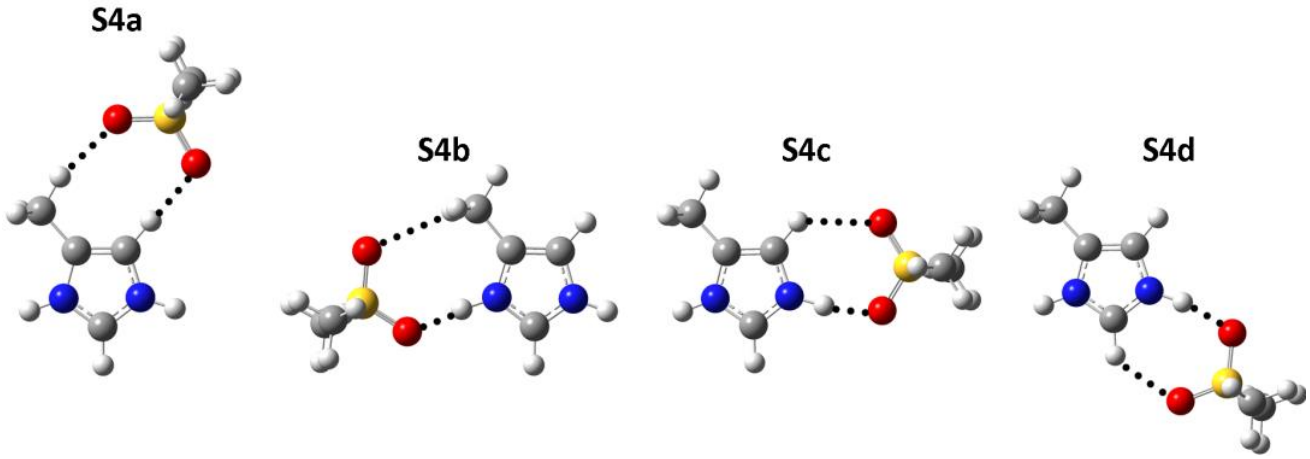

Fig. S4. Optimized geometries of the Me_2SO_2-4-methylimidazolium conformers at the MP2(full)/6-311++G(d,p) level of theory in the gas phase. See Fig. S1 for details of the structure representation and the atomic coordinates are provided starting on page S11. The global minimum conformer **2b** is shown in Fig. 2 of the main text but not here.

Table S4. Ab initio equilibrium distance (r_{SX}, Å), angle (θ_{SXY}, degrees), binding energy (E and E^{CP}, kcal/mol), net charge of Me_2SO_2 in the cationic complexes (e), IPV (eV), sum of Mulliken atomic spin densities for Me_2SO_2 in the (+2) radicals, and the MM binding energy calculated with the default FF (E^{MM}, kcal/mol) for the Me_2SO_2-4-methylimidazolium conformers in Fig. S4

Conformer	r_{SX}	θ_{SXY}	E	E^{CP}	E^{MM}	Me_2SO_2 charge	Me_2SO_2 spin density	IPV [a]
S4a	5.045	90	−18.93	−15.81	−19.46	0.03	0.0	13.70
S4b	4.873	84	−27.52	−23.32	−24.75	0.06	0.0	13.54
S4c	4.582	90	−27.93	−23.89	−24.27	0.06	0.0	13.51
S4d	4.562	90	−28.40	−24.46	−25.77	0.06	0.0	13.52
2b [b]	4.557	90	−28.58	−24.50	−25.83	0.06	0.0	13.52

[a] The IPV of free 4-methylimidazolium is 14.64 eV (see Footnote c to Table 2 of the main text).

[b] The structure of the global minimum conformer **2b** is shown in Fig. 2 of the main text.

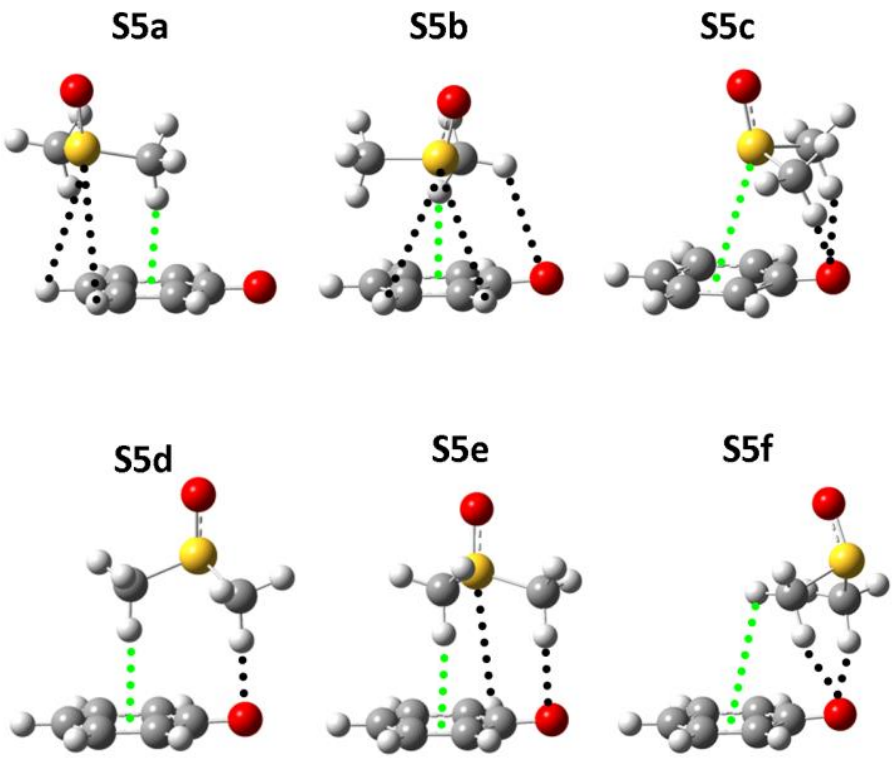

Fig. S5. Optimized geometries of the Me_2SO-phenolate conformers at the MP2(full)/6-311++G(d,p) level of theory in the gas phase. See Fig. S1 for details of the structure representation. Dotted green lines show intermolecular π-type H-bonds. The atomic coordinates are provided starting on page S11. The global minimum conformer **1c** is shown in Fig. 2 of the main text but not here. Note that **S5a**-**S5e** are stabilized by σ-hole···π_{ar} interactions; σ-hole···O_{ar} interaction stabilizes **S5f**.

Table S5. Ab initio equilibrium distance (r_{SX}, Å), angle (θ_{SXY}, degrees), binding energy (E and E^{CP}, kcal/mol), net charge of Me_2SO (e), IPV (eV), sum of Mulliken atomic spin densities for Me_2SO in the neutral radicals, and the MM binding energy calculated with the default FF (E^{MM}, kcal/mol) for the Me_2SO-phenolate conformers in Fig. S5

Conformer	r_{SX}	θ_{SXY}	E	E^{CP}	E^{MM}	*Me_2SO charge*	*Me_2SO spin density*	*IPV* [a]
S5a	4.005	26	−19.32	−13.76	−16.65	−0.02	0.0	4.01
S5b	3.965	27	−19.76	−13.92	−16.00	−0.02	0.0	4.01
S5c	3.446	16	−23.48	−16.90	−16.63	− 0.04	0.0	4.13
S5d	4.287	24	−23.06	−17.00	−16.62	−0.03	0.0	4.17
S5e	4.021	31	−23.58	−17.18	−16.84	−0.03	0.0	4.17
S5f	4.973	37	−22.28	−17.47	−16.57	−0.04	0.0	4.16
1c [b]	5.455	84	−22.01	−18.09	−16.82	−0.03	0.0	4.10

[a] The IPV of free phenolate is 3.41 eV (see Footnote c to Table 2 of the main text).

[b] The structure of the global minimum conformer **1c** is shown in Fig. 2 of the main text.

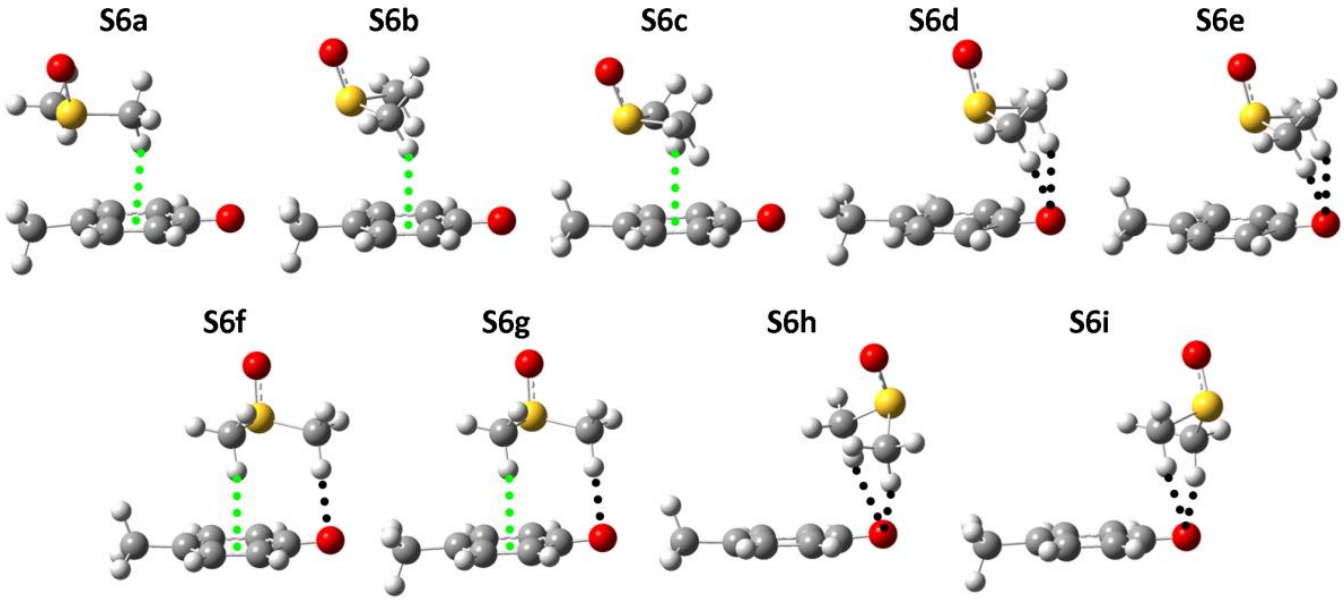

Fig. S6. Optimized geometries of the Me_2SO-4-methylphenolate conformers at the MP2(full)/6-311++G(d,p) level of theory in the gas phase. See Fig. S1 for details of the structure representation. Dotted green lines show intermolecular π-type H-bonds. The atomic coordinates are provided starting on page S11. The global minimum conformer **1d** is shown in Fig. 2 of the main text but not here. Note that **S6a**-**S6g** are stabilized by σ-hole···π_{ar} interactions; σ-hole···O_{ar} interactions stabilize **S6h** and **S6i**.

Table S6. Ab initio equilibrium distance (r_{SX}, Å), angle (θ_{SXY}, degrees), binding energy (E and E^{CP}, kcal/mol), net charge of Me_2SO (e), IPV (eV), sum of Mulliken atomic spin densities for Me_2SO in the neutral radicals, and the MM binding energy calculated with the default FF (E^{MM}, kcal/mol) for the Me_2SO-4-methylphenolate conformers in Fig. S6

Conformer	r_{SX}	θ_{SXY}	E	E^{CP}	E^{MM}	Me_2SO charge	Me_2SO spin density	IPV[a]
S6a	3.862	29	−20.69	−14.45	−16.42	-0.01	0.0	3.89
S6b	3.909	30	−20.66	−14.58	−16.22	-0.01	0.0	3.91
S6c	3.905	30	−20.90	−14.67	−16.36	-0.01	0.0	3.91
S6d	3.367	13	−23.85	−17.09	−16.66	-0.04	0.0	4.01
S6e	3.353	13	−23.90	−17.10	−16.67	-0.03	0.0	4.01
S6f	3.963	30	−23.79	−17.34	−16.95	-0.03	0.0	4.05
S6g	3.977	30	−23.77	−17.40	−16.95	-0.03	0.0	4.05
S6h	4.982	40	−22.41	−17.66	−16.55	-0.04	0.0	4.04
S6i	5.096	43	−22.40	−17.82	−16.49	-0.04	0.0	4.05
1d [b]	5.481	87	−22.06	−18.25	−16.93	-0.03	0.0	3.98

[a] The IPV of free 4-methylphenolate is 3.31 eV (see Footnote c to Table 2 of the main text).

[b] The structure of the global minimum conformer **1d** is shown in Fig. 2 of the main text.

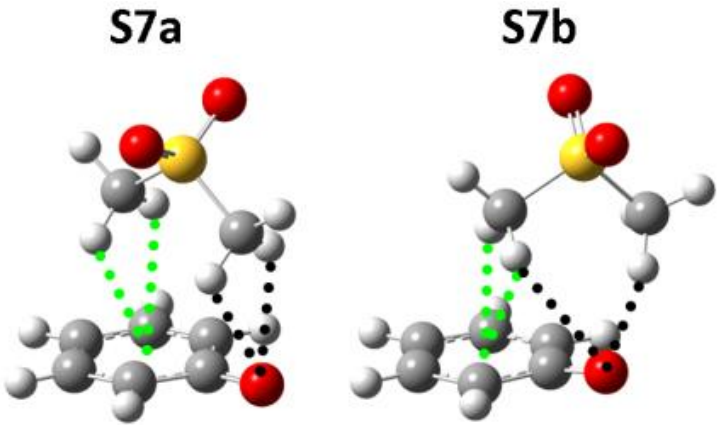

Fig. S7. Optimized geometries of the Me_2SO_2-phenolate conformers at the MP2(full)/6-311++G(d,p) level of theory in the gas phase. See Fig. S1 for details of the structure representation. Dotted green lines show intermolecular π-type H-bonds. The atomic coordinates are provided starting on page S11. The global minimum conformer **2c** is shown in Fig. 2 of the main text but not here. Note that **S7a** and **S7b** are stabilized by σ-hole···π_{ar} interactions; σ-hole···O_{ar} interaction additionally stabilizes **S7b**.

Table S7. Ab initio equilibrium distance (r_{SX}, Å), angle (θ_{SXY}, degrees), binding energy (E and E^{CP}, kcal/mol), net charge of Me_2SO_2 (e), IPV (eV), sum of Mulliken atomic spin densities for Me_2SO_2 in the neutral radicals, and the MM binding energy calculated with the default FF (E^{MM}, kcal/mol) for the Me_2SO_2-phenolate conformers in Fig. S7

Conformer	r_{SX}	θ_{SXY}	E	E^{CP}	E^{MM}	Me_2SO_n charge	Me_2SO_n spin density	IPV [a]
S7a	4.387	16	−24.64	−19.39	−23.89	−0.03	0.0	4.27
S7b	4.513	26	−26.20	−20.52	−23.47	−0.03	0.0	4.29
2c [b]	4.839	36	−25.54	−20.73	−21.70	−0.04	0.0	4.29

[a] The IPV of free phenolate is 3.41 eV (see Footnote c to Table 2 of the main text).

[b] The structure of the global minimum conformer **2c** is shown in Fig. 2 of the main text.

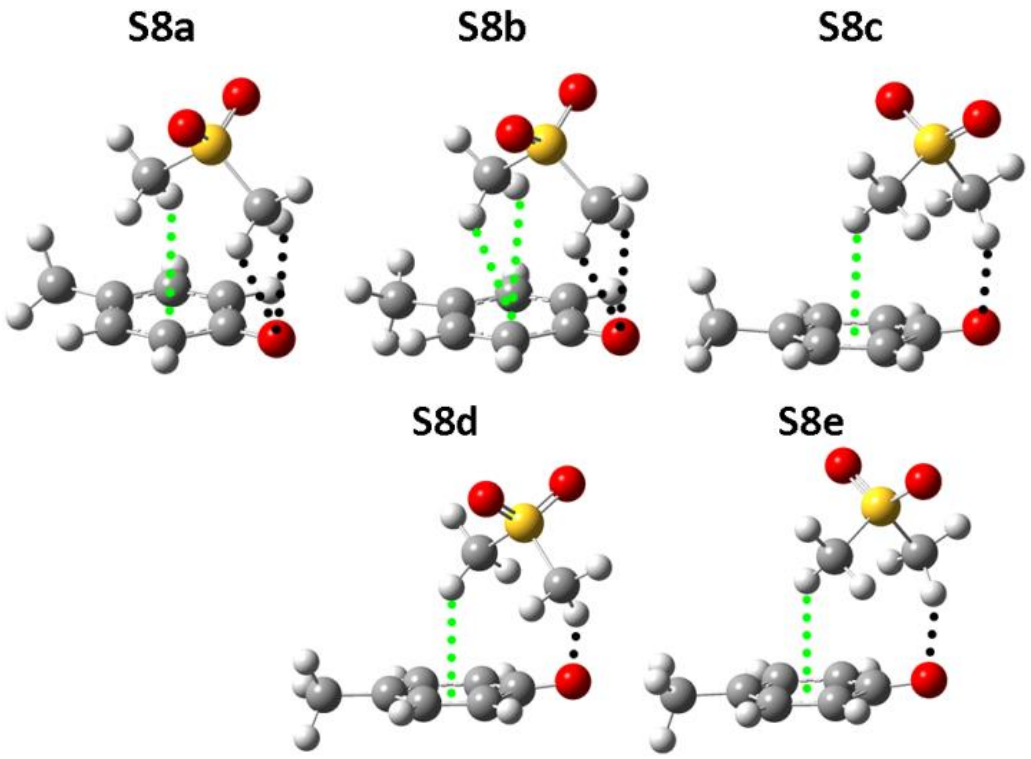

Fig. S8. Optimized geometries of the Me_2SO_2-4-methylphenolate conformers at the MP2(full)/6-311++G(d,p) level of theory in the gas phase. See Fig. S1 for details of the structure representation. Dotted green lines show intermolecular π-type H-bonds. The atomic coordinates are provided starting on page S11. The global minimum conformer **2d** is shown in Fig. 2 of the main text but not here. Note that **S8a**-**S8e** are stabilized by σ-hole···π_{ar} interactions; σ-hole···O_{ar} interactions additionally stabilize **S8c**-**S8e**.

Table S8. Ab initio equilibrium distance (r_{SX}, Å), angle (θ_{SXY}, degrees), binding energy (E and E^{CP}, kcal/mol), net charge of Me_2SO_2 (e), IPV (eV), sum of Mulliken atomic spin densities for Me_2SO_2 in the neutral radicals, and the MM binding energy calculated with the default FF (E^{MM}, kcal/mol) for the Me_2SO_2-4-methylphenolate conformers in Fig. S8

Conformer	r_{SX}	θ_{SXY}	E	E^{CP}	E^{MM}	Me_2SO_2 charge	Me_2SO_2 spin density	IPV [a]
S8a	4.365	16	−24.84	−19.47	−23.86	-0.02	0.0	4.15
S8b	4.373	17	−24.83	−19.60	−23.96	-0.02	0.0	4.15
S8c	4.473	23	−26.38	−20.63	−23.54	-0.03	0.0	4.17
S8d	4.474	25	−26.43	−20.68	−23.64	-0.03	0.0	4.16
S8e	4.492	25	−26.30	−20.71	−23.56	-0.03	0.0	4.16
2d [b]	4.881	39	−25.77	−21.03	−22.63	-0.04	0.0	4.17

[a] The IPV of free 4-methylphenolate is 3.31 eV (see Footnote c to Table 2 of the main text).

[b] The structure of the global minimum conformer **2d** is shown in Fig. 2 of the main text.

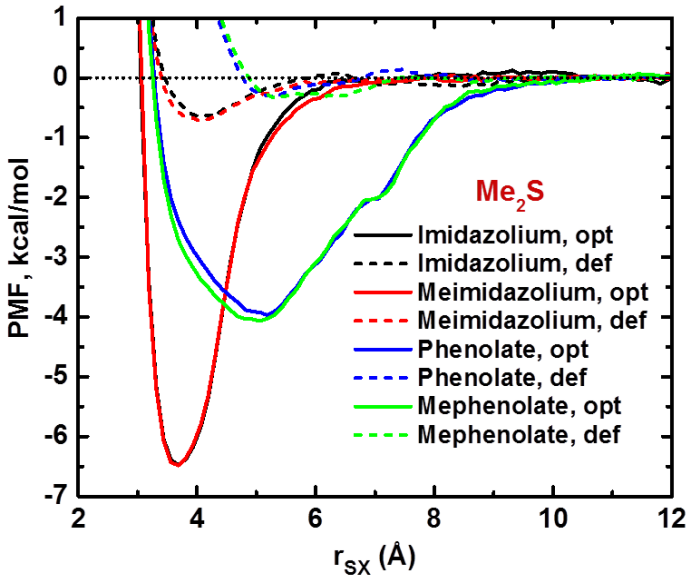

Fig. S9. Potential of mean force (PMF, kcal/mol) as a function of distance between the S atom of (A) Me_2S and the ring centroid X (r_{SX}, Å) of imidazolium ion (black), 4-methylimidazolium ion (red), phenolate ion (blue), and 4-methylphenolate ion (green) in bulk water at 298.15 K. Solid curves were calculated using our previous optimized pair specific LJ parameters for the Me_2S-aromatic ions and for H_2O-phenolate (see Ref. 18 of the main text) plus revised parameters for Me_2S-H_2O interactions optimized in a previous work (see Ref. 19 of the main text). The dashed curves are calculated with the default FF parameters (i.e., without pair specific LJ parameters between any pair).

Notably, the default parameters in Fig. S9 predict very weak Me_2S affinity for the ions in water (−0.3 to −0.7 kcal/mol), which we attribute to underestimation of their gas-phase affinities (Ref. 18 of the main text). The optimized FF for Me_2S-imidazoliums (Ref. 18 of the main text) and for Me_2S-H_2O (Ref. 19 of the main text) gives a binding free energy for Me_2S-imidazolium of -6.0 kcal/mol and for Me_2S-phenolate of −3.9 kcal/mol.

Atomic coordinates of the global minimum conformers in Fig. 2

Conformer 1a

C	3.178405	0.213642	-1.354470
H	3.209679	1.299570	-1.250712
H	4.181203	-0.218571	-1.335621
H	2.674831	-0.063778	-2.280569
S	2.223701	-0.465948	-0.001043
C	3.177365	0.207825	1.356009
H	3.208442	1.294213	1.257086
H	2.673275	-0.073798	2.280562
H	4.180280	-0.224061	1.335907
O	0.920443	0.360908	0.000183
C	-2.395798	-1.131331	-0.002283
C	-3.702569	-0.705383	-0.001382
C	-2.370556	1.073074	0.002133
N	-1.599805	-0.013621	-0.000123
H	-0.522821	0.024386	-0.000156
H	-1.989161	-2.129914	-0.004304
H	-4.631248	-1.253005	-0.002427
H	-2.027139	2.095515	0.004160
N	-3.652790	0.668132	0.001358
H	-4.453013	1.288811	0.002627

Conformer 1b

C	-3.679485	0.032528	1.355389
H	-3.796922	1.114727	1.277202
H	-4.644771	-0.477361	1.323560
H	-3.156340	-0.225490	2.276248
S	-2.671198	-0.536266	-0.010817
C	-3.676995	0.090475	-1.353307
H	-3.794812	1.168324	-1.229102
H	-3.152114	-0.127839	-2.283403
H	-4.642250	-0.420405	-1.345173
O	-1.438432	0.389468	0.010302
C	2.002017	-0.823826	-0.010812
C	3.279389	-0.306079	-0.004428
C	1.797834	1.369492	0.019809
N	1.116975	0.225551	0.004335
H	0.046262	0.175373	0.004342
H	1.675128	-1.851615	-0.024603
H	1.374813	2.361559	0.034133
N	3.108425	1.063376	0.014583
H	3.856530	1.746382	0.023624
C	4.616301	-0.962816	-0.014486
H	5.189449	-0.674662	-0.899417
H	5.190503	-0.699774	0.877550
H	4.488985	-2.045848	-0.029719

Conformer 1c

C	2.766391	-1.519456	-0.326172
C	3.979479	-0.870050	-0.051572
C	3.946406	0.512774	0.188778
C	2.738399	1.210663	0.225599
C	1.477321	0.586567	-0.058124
C	1.553387	-0.829479	-0.288308
H	2.760987	-2.591944	-0.523047
H	0.622160	-1.348654	-0.512787
H	4.922893	-1.408977	-0.088043
H	4.874567	1.045513	0.398436
H	2.727782	2.283072	0.415276
O	0.363227	1.229315	-0.066269
C	-2.589000	1.177562	-0.883821
H	-3.200757	1.850254	-0.276025
H	-1.530937	1.463859	-0.886026
H	-2.995620	1.120555	-1.895306
S	-2.700876	-0.470116	-0.178006
C	-2.003069	-0.043129	1.419389
H	-2.669637	0.678540	1.900261
H	-1.955862	-0.958941	2.010821
H	-1.006043	0.375180	1.228077
O	-4.182150	-0.771730	0.031499

Conformer 1d

C	2.456268	-1.202209	-0.206315
C	3.619026	-0.437071	-0.018498
C	3.445293	0.946294	0.157076
C	2.179074	1.534184	0.183612
C	0.973910	0.782551	-0.017091
C	1.183297	-0.628241	-0.180029
H	2.547661	-2.281789	-0.342622
H	0.301887	-1.250604	-0.332565
H	4.324922	1.575196	0.310000
H	2.076088	2.608987	0.327327
O	-0.197633	1.316248	-0.017282
C	4.992361	-1.055624	-0.098260
H	5.391178	-1.059185	-1.122030
H	5.707662	-0.508641	0.526900
H	4.976400	-2.095594	0.247665
C	-3.081309	1.014300	-0.977183
H	-3.774370	1.675463	-0.449168
H	-2.047411	1.377428	-0.940253
H	-3.422183	0.864778	-2.003404
S	-3.116885	-0.590077	-0.171032
C	-2.542723	-0.014487	1.429052
H	-3.281679	0.689040	1.823297
H	-2.471881	-0.885560	2.082629
H	-1.564703	0.457041	1.263159
O	-4.582940	-0.986687	-0.018794

Conformer 2a

C	-2.859334	-1.183300	-0.000972
C	-3.867279	-0.250113	0.000125
C	-1.917285	0.823808	0.000117
N	-1.675065	-0.489174	-0.000843
H	-0.710474	-0.878821	-0.002008
H	-2.898710	-2.260690	-0.001905
H	-4.939510	-0.362306	0.000368
H	-1.162562	1.596827	0.000639
N	-3.250151	0.979361	0.000797
H	-3.720536	1.876438	0.001593
C	2.903675	-0.080259	1.405553
H	3.432334	-1.033398	1.376344
H	3.591460	0.765823	1.392019
H	2.259955	-0.030589	2.285030
C	2.908986	-0.074943	-1.402114
H	3.438573	-1.027588	-1.373850
H	2.268440	-0.023320	-2.283806
H	3.595716	0.771889	-1.383412
O	0.964227	-1.168463	-0.004144
S	1.833338	0.029734	-0.000135
O	1.157753	1.329403	0.001045

Conformer 2b

C	2.711025	0.619578	-0.000150
C	3.596532	-0.435795	-0.000024
C	1.538917	-1.280030	0.000134
N	1.454157	0.053449	-0.000149
H	0.546041	0.555492	-0.000510
H	4.674870	-0.449491	-0.000086
H	0.700045	-1.960398	0.000117
N	2.843596	-1.588214	0.000095
H	3.207392	-2.533241	0.000152
C	2.935054	2.092176	-0.000046
H	2.491229	2.552063	-0.886271
H	2.494309	2.551529	0.888003
H	4.005319	2.302092	-0.001844
C	-3.151755	0.226215	1.403895
H	-3.563372	1.235453	1.375803
H	-3.935362	-0.531930	1.387926
H	-2.520411	0.098664	2.284526
C	-3.153818	0.225294	-1.402627
H	-3.565426	1.234533	-1.374522
H	-2.523764	0.097248	-2.284113
H	-3.937358	-0.532881	-1.385024
O	-1.093491	1.077223	-0.001236
S	-2.098776	-0.008538	-0.000077
O	-1.585646	-1.380199	0.000032

Conformer 2c

C	-2.900012	-0.837454	1.082464
C	-2.055249	0.257507	1.273127
C	-1.545692	1.042778	0.180826
C	-2.087956	0.686613	-1.103115
C	-2.932776	-0.409593	-1.285124
C	-3.371839	-1.177367	-0.195069
H	-1.710638	0.515290	2.274286
H	-3.237016	-1.406023	1.949832
H	-4.022170	-2.035889	-0.341173
H	-3.295320	-0.640403	-2.287347
H	-1.766667	1.278887	-1.959608
O	-0.678221	1.975428	0.336803
C	1.309879	-0.195018	1.381960
H	0.811284	0.780310	1.393383
H	0.570300	-0.993289	1.313168
H	1.968493	-0.341849	2.239894
C	1.247198	0.180558	-1.365088
H	0.775111	1.132884	-1.103626
H	1.861623	0.247965	-2.264721
H	0.489522	-0.597356	-1.464390
O	3.371213	0.789433	0.069410
S	2.352491	-0.260503	-0.050680
O	2.798795	-1.647438	-0.251052

Conformer 2d

C	1.602229	-0.857702	1.209080
C	2.662636	0.051403	1.198184
C	3.203784	0.546646	0.000039
C	2.678712	0.025159	-1.194185
C	1.618377	-0.883879	-1.199218
C	1.017108	-1.385229	0.006542
H	1.218730	-1.235400	2.156788
H	3.062388	0.410577	2.148869
H	3.091285	0.363363	-2.147066
H	1.245970	-1.281147	-2.143367
O	0.019880	-2.195133	0.008280
C	4.312611	1.569210	-0.003735
H	4.956744	1.448513	-0.882195
H	3.930660	2.599067	-0.018276
H	4.943995	1.468835	0.886460
C	-1.664378	0.031491	1.390814
H	-1.299019	-0.991128	1.244420
H	-0.824670	0.725248	1.440233
H	-2.307484	0.128920	2.267315
C	-1.622506	0.069879	-1.380654
H	-1.276208	-0.962152	-1.260785
H	-2.233778	0.209120	-2.274126
H	-0.771734	0.751914	-1.376323
O	-3.826322	-0.450918	-0.034998
S	-2.672208	0.455667	-0.004798
O	-2.922681	1.905018	0.010919

Local minimum Me_2SO-imidazolium conformers (Fig. S1)

Conformer S1a

C	3.155648	0.191515	-1.384270
H	2.909126	1.253917	-1.435410
H	4.235955	0.038554	-1.333677
H	2.752365	-0.330069	-2.252547
S	2.383148	-0.519311	0.073133
C	3.140243	0.569575	1.284512
H	2.895574	1.604036	1.035242
H	2.725706	0.309453	2.258731
H	4.220731	0.409872	1.291262
O	0.910964	-0.116020	0.007495
C	-1.779602	0.677037	-0.079850
C	-1.838168	-0.684464	0.082103
C	-3.929553	0.085725	-0.012613
N	-3.081400	1.116941	-0.134120
H	-3.373418	2.080539	-0.249229
H	-0.914093	1.314963	-0.155355
H	-1.028804	-1.390350	0.166319
H	-5.006843	0.131350	-0.018930
N	-3.172846	-1.013047	0.118989
H	-3.546069	-1.948711	0.230136

Conformer S1b

C	3.179348	0.229524	-1.354204
H	3.183483	1.315794	-1.249033
H	4.192569	-0.177689	-1.335397
H	2.683180	-0.058619	-2.281019
S	2.240923	-0.474861	-0.001932
C	3.179387	0.218493	1.356005
H	3.183325	1.305592	1.259764
H	2.683380	-0.077346	2.280477
H	4.192675	-0.188377	1.333723
O	0.919582	0.321086	0.001333
C	-2.384735	1.130982	0.004290
C	-3.698100	0.726639	0.002751
C	-2.395563	-1.074220	-0.004068
N	-1.607498	0.000325	0.000008
H	-0.531777	0.003230	0.000043
H	-1.953585	2.119185	0.008039
H	-4.618189	1.288628	0.004878
H	-2.076512	-2.104391	-0.007970
N	-3.671133	-0.647559	-0.002455
H	-4.481585	-1.254783	-0.004767

Local minimum Me_2SO-4-methylimidazolium conformers (Fig. S2)

Conformer S2a

C	3.446616	-0.333101	1.372503
H	3.130590	-1.376242	1.435677
H	4.532099	-0.253462	1.280816
H	3.112231	0.214571	2.253898
S	2.669158	0.428679	-0.055856
C	3.304039	-0.707992	-1.293817
H	3.004280	-1.724465	-1.030999
H	2.868113	-0.421324	-2.251142
H	4.391470	-0.618514	-1.344543
O	1.176012	0.123841	0.068174
C	-1.595108	-0.617180	-0.013274
C	-2.158987	0.639909	0.019351
C	-3.811068	-0.877530	0.008993
N	-2.634671	-1.517583	-0.018538
H	-2.538408	-2.525939	-0.038021
H	-4.791903	-1.325554	0.011574
N	-3.524963	0.432962	0.031639
H	-4.225565	1.165387	0.055368
H	-0.544878	-0.882238	-0.026888
C	-1.516497	1.981481	0.041092
H	-1.793290	2.563403	-0.841926
H	-1.803197	2.538335	0.936974
H	-0.436402	1.825283	0.046005

Conformer S2b

C	-3.417210	0.261480	1.349545
H	-3.188377	1.324505	1.251408
H	-4.494845	0.084700	1.326933
H	-3.000845	-0.128385	2.278634
S	-2.637708	-0.629709	-0.000745
C	-3.417508	0.265041	-1.348503
H	-3.188235	1.327732	-1.247788
H	-3.001702	-0.122624	-2.278761
H	-4.495197	0.088598	-1.325841
O	-1.174198	-0.183253	-0.000343
C	2.123895	0.683811	0.000367
C	1.653114	-0.610873	-0.000296
C	3.882170	-0.707695	-0.000342
N	3.501464	0.579043	0.000319
H	4.147483	1.360351	0.000732
H	0.619884	-0.943151	-0.000530
H	4.893259	-1.082518	-0.000519
N	2.755485	-1.432348	-0.000689
H	2.732237	-2.445282	-0.001185
C	1.380091	1.972591	0.001010
H	1.616894	2.561927	0.890720
H	1.616922	2.562820	-0.888100
H	0.313481	1.739690	0.000866

Conformer S2c

C	3.640907	-0.390700	1.351577
H	3.555561	-1.472834	1.238263
H	4.684254	-0.068251	1.335870
H	3.169702	-0.070071	2.280770
S	2.762987	0.398633	0.005014
C	3.644791	-0.358829	-1.357215
H	3.558921	-1.443313	-1.269712
H	3.176387	-0.016249	-2.279966
H	4.688136	-0.037076	-1.330783
O	1.381515	-0.284350	-0.005116
C	-1.996133	-0.818618	-0.006949
C	-3.279588	-0.316610	-0.002537
C	-1.818437	1.377764	0.010523
N	-1.124206	0.241385	0.001240
H	-0.057893	0.150327	0.000032
H	-1.414437	2.377728	0.018438
H	-1.648687	-1.839657	-0.015366
N	-3.125458	1.055015	0.008413
H	-3.881948	1.728742	0.013954
C	-4.608719	-0.989040	-0.007420
H	-4.468073	-2.070470	-0.016201
H	-5.185194	-0.727568	0.883621
H	-5.185926	-0.713235	-0.893653

Conformer S2d

C	3.366600	-0.232474	1.355388
H	3.479489	-1.313294	1.254515
H	4.334341	0.273465	1.336988
H	2.841968	0.008497	2.280058
S	2.363665	0.369531	-0.000704
C	3.366646	-0.236935	-1.354772
H	3.479483	-1.317426	-1.250366
H	2.842080	0.001041	-2.280253
H	4.334407	0.269022	-1.337963
O	1.124671	-0.547472	0.000782
C	-2.274402	0.744256	-0.000472
C	-3.558994	0.245097	-0.000257
C	-2.151494	-1.471865	0.000992
N	-1.434707	-0.347698	0.000297
H	-0.364324	-0.326074	0.000467
H	-1.760812	-2.477219	0.001681
N	-3.449396	-1.125909	0.000625
H	-4.220401	-1.782207	0.000941
H	-4.512551	0.748939	-0.000679
C	-1.771543	2.147025	-0.001275
H	-1.165495	2.343147	0.886730
H	-1.164315	2.341702	-0.888789
H	-2.612032	2.842326	-0.002406

Conformer S2e

C	-3.338152	0.178082	1.356477
H	-3.280713	1.263938	1.262801
H	-4.372982	-0.170424	1.334093
H	-2.859495	-0.147500	2.280148
S	-2.439950	-0.564428	-0.003340
C	-3.338492	0.196190	-1.352884
H	-3.280896	1.280688	-1.244747
H	-2.860124	-0.117112	-2.280939
H	-4.373349	-0.152498	-1.334868
O	-1.074076	0.151537	0.001291
C	2.275804	0.749408	0.002027
C	3.563208	0.257157	0.001579
C	2.165951	-1.468812	-0.004304
N	1.442796	-0.348128	-0.001834
H	0.376116	-0.282081	-0.001610
H	1.787934	-2.478842	-0.007283
N	3.461996	-1.114449	-0.002285
H	4.237035	-1.765864	-0.003479
H	4.514161	0.765937	0.003788
C	1.759303	2.146605	0.004938
H	1.151257	2.333722	-0.882864
H	1.139909	2.325636	0.886511
H	2.593678	2.849210	0.013399

Local minimum Me_2SO_2-imidazolium conformers (Fig. S3)

Conformer S3a

C	1.862132	-0.706906	0.000039
C	1.833658	0.666551	-0.000216
C	3.969450	0.023391	0.000073
N	3.189473	-1.066303	0.000125
H	3.540488	-2.017219	0.000306
H	1.041370	-1.409525	0.000126
H	0.984396	1.335622	-0.000421
H	5.047642	0.045575	0.000126
N	3.145146	1.079925	-0.000093
H	3.456409	2.044600	-0.000162
C	-3.002873	-0.010645	-1.401315
H	-3.603517	-0.920209	-1.379128
H	-3.623695	0.885278	-1.379413
H	-2.362207	-0.003492	-2.284294
C	-3.003045	-0.009721	1.401227
H	-3.603711	-0.919283	1.379545
H	-2.362497	-0.002011	2.284285
H	-3.623849	0.886198	1.378653
O	-1.144686	-1.247491	0.000476
S	-1.915024	0.001919	0.000019
O	-1.173903	1.269040	-0.000351

Conformer S3b

C	-1.976126	0.916986	-0.000114
C	-3.346565	1.011162	-0.000128
C	-2.792889	-1.143878	0.000067
N	-1.671071	-0.422432	0.000124
H	-0.697788	-0.798977	0.000067
H	-1.201571	1.669010	-0.000144
H	-4.000625	1.868216	-0.000207
H	-2.864705	-2.219984	0.000156
N	-3.821168	-0.279794	-0.000040
H	-4.797426	-0.550477	-0.000048
C	2.919859	-0.115575	1.404135
H	3.408400	-1.089833	1.375795
H	3.642171	0.701202	1.388281
H	2.280244	-0.036583	2.284473
C	2.921718	-0.116218	-1.402832
H	3.410186	-1.090476	-1.373405
H	2.283276	-0.037600	-2.284058
H	3.644021	0.700553	-1.386367
O	0.939124	-1.128868	-0.000495
S	1.852450	0.039084	-0.000101
O	1.228914	1.361409	-0.000789

Local minimum Me_2SO_2-4-methylimidazolium conformers (Fig. S4)

Conformer S4a

C	-1.677795	-0.554778	0.000386
C	-2.284270	0.683249	-0.000025
C	-3.882748	-0.892355	-0.000079
N	-2.685859	-1.490938	0.000307
H	-2.548644	-2.495215	0.000522
H	-0.629798	-0.831011	0.000658
H	-4.847738	-1.373811	-0.000213
N	-3.642825	0.427094	-0.000256
H	-4.368190	1.135538	-0.000578
C	-1.709895	2.056735	-0.000078
H	-2.025370	2.609551	-0.888870
H	-2.024561	2.609266	0.889181
H	-0.621290	1.983983	-0.000574
C	3.287839	-0.141930	1.400565
H	3.831810	-1.086496	1.378697
H	3.962409	0.714315	1.377915
H	2.649334	-0.094844	2.283894
C	3.287283	-0.143775	-1.400910
H	3.831235	-1.088327	-1.378027
H	2.648431	-0.097812	-2.284048
H	3.961885	0.712479	-1.379630
O	1.364707	-1.272492	0.000951
S	2.201533	-0.063240	-0.000007
O	1.527076	1.237273	-0.000741

Conformer S4b

C	2.271298	0.734129	-0.029900
C	3.611642	0.433006	-0.142490
C	2.514854	-1.471958	0.177461
N	1.630726	-0.471322	0.168641
H	0.601830	-0.604138	0.275702
H	4.465039	1.072493	-0.303283
H	2.295590	-2.519845	0.307938
N	3.727945	-0.931130	-0.010551
H	4.591525	-1.458747	-0.051142
C	1.556248	2.040881	-0.062940
H	0.678978	1.991742	-0.710885
H	1.223265	2.322991	0.939362
H	2.228387	2.816515	-0.432467
C	-3.087681	-0.953923	-1.188083
H	-3.400110	-1.887804	-0.720313
H	-3.941311	-0.348383	-1.494286
H	-2.442719	-1.153690	-2.045075
C	-3.183492	0.261069	1.341882
H	-3.497462	-0.697035	1.756463
H	-2.596767	0.818279	2.073734
H	-4.034011	0.856987	1.009287
O	-1.018784	-0.910779	0.430579
S	-2.111013	-0.023340	-0.039299
O	-1.731708	1.251030	-0.637887

Conformer S4c

C	1.687215	-0.499771	-0.000192
C	3.063759	-0.442721	-0.000099
C	2.247358	1.643210	-0.000320
N	1.220903	0.792858	-0.000184
H	0.212068	1.048510	-0.000167
H	2.190576	2.720197	-0.000440
N	3.370447	0.904121	-0.000182
H	4.307296	1.290451	-0.000047
H	1.007769	-1.338972	-0.000135
C	4.098264	-1.514183	-0.000159
H	4.730739	-1.449852	-0.889209
H	4.731505	-1.449244	0.888298
H	3.609086	-2.488837	0.000390
C	-3.304313	-0.104798	1.403837
H	-3.916025	0.797207	1.375111
H	-3.913625	-1.008981	1.388309
H	-2.660196	-0.098947	2.284436
C	-3.305420	-0.105250	-1.402779
H	-3.916978	0.796854	-1.373957
H	-2.661991	-0.099870	-2.283881
H	-3.914848	-1.009341	-1.386390
O	-1.472298	1.157518	-0.000412
S	-2.224475	-0.118817	0.000103
O	-1.437002	-1.350754	0.000020

Conformer S4d

C	-2.429174	-1.082557	-0.000120
C	-3.423611	-0.129168	-0.000056
C	-1.429991	0.894484	0.000117
N	-1.224151	-0.423637	-0.000008
H	-0.273472	-0.840005	-0.000036
H	-0.655672	1.647704	0.000201
N	-2.759959	1.082555	0.000116
H	-3.205211	1.992696	0.000212
H	-2.497229	-2.158842	-0.000245
C	-4.908248	-0.247501	-0.000025
H	-5.339317	0.219668	0.889059
H	-5.339453	0.220865	-0.888412
H	-5.188802	-1.301357	-0.000723
C	3.379505	-0.125020	1.403289
H	3.885816	-1.090198	1.374341
H	4.086648	0.704868	1.387131
H	2.739201	-0.059271	2.284216
C	3.379378	-0.124208	-1.403445
H	3.885697	-1.089400	-1.375098
H	2.738992	-0.057959	-2.284275
H	4.086517	0.705676	-1.386878
O	1.411741	-1.168869	-0.000291
S	2.308005	0.008038	0.000009
O	1.666987	1.324910	0.000423

Local minimum Me_2SO-phenolate conformers (Fig. S5)

Conformer S5a

C	-1.978982	-0.515445	1.139016
C	-2.490975	-0.610175	-0.211009
C	-2.146601	0.525913	-1.039448
C	-1.394605	1.605847	-0.572726
C	-0.898127	1.638839	0.742041
C	-1.217244	0.561902	1.588871
H	-2.214278	-1.338808	1.812802
H	-0.856364	0.564897	2.618126
H	-0.325031	2.487832	1.107206
H	-1.189292	2.439024	-1.247815
H	-2.517572	0.518615	-2.063949
O	-3.168613	-1.598346	-0.632269
C	2.242520	1.101462	-0.934965
H	2.526546	0.646287	-1.887641
H	1.246243	1.544478	-0.978434
H	2.985898	1.846013	-0.644686
S	2.251252	-0.188342	0.324995
C	1.000088	-1.208320	-0.458830
H	1.375309	-1.512383	-1.439968
H	0.845007	-2.084416	0.171710
H	0.065175	-0.648364	-0.532443
O	3.586348	-0.907884	0.178202

Conformer S5b

C	-2.446419	-0.224093	-0.879937
C	-2.241279	1.152844	-0.972024
C	-1.590124	1.866426	0.051109
C	-1.166295	1.146456	1.182544
C	-1.358522	-0.231497	1.281253
C	-1.953924	-1.017049	0.223861
H	-2.943089	-0.759784	-1.688323
H	-2.608876	1.687622	-1.849038
H	-1.451809	2.943102	-0.015926
H	-0.690624	1.675210	2.010505
H	-1.004157	-0.771972	2.158159
O	-2.032179	-2.285254	0.259646
C	2.168293	1.501803	-0.118570
H	2.533328	1.612123	-1.143512
H	1.169431	1.927479	-0.001300
H	2.872799	1.962968	0.576135
S	2.106572	-0.259528	0.271535
C	0.997824	-0.693222	-1.075077
H	1.563251	-0.584253	-2.005350
H	0.674260	-1.725567	-0.933349
H	0.121918	-0.042852	-1.047211
O	3.482315	-0.812451	-0.080185

Conformer S5c

C	2.328499	-1.548397	-0.000017
C	2.073109	-0.873306	1.203206
C	1.573790	0.429870	1.207110
C	1.255407	1.143551	-0.000047
C	1.573738	0.429770	-1.207172
C	2.073146	-0.873390	-1.203306
H	2.705745	-2.567837	0.000053
H	2.277472	-1.368268	2.153140
H	1.386406	0.942824	2.150215
H	2.277415	-1.368393	-2.153232
H	1.386354	0.942637	-2.150330
O	0.701430	2.302139	-0.000022
C	-1.749920	0.638027	-1.327799
H	-2.758235	1.061337	-1.283176
H	-0.978753	1.402725	-1.187875
H	-1.610791	0.106159	-2.270410
S	-1.614492	-0.572512	0.000023
C	-1.749252	0.638272	1.327664
H	-2.757784	1.061173	1.283816
H	-1.609014	0.106763	2.270308
H	-0.978574	1.403330	1.186688
O	-2.923864	-1.360718	0.000346

Conformer S5d

C	2.266369	-0.998446	-1.101025
C	1.722432	0.270845	-1.302729
C	1.438140	1.178461	-0.219412
C	1.787435	0.666146	1.082559
C	2.336872	-0.602877	1.273381
C	2.576782	-1.462578	0.188615
H	2.451732	-1.640340	-1.962941
H	1.481959	0.613487	-2.308390
H	1.608326	1.320946	1.934967
H	2.577632	-0.932075	2.284847
H	3.002902	-2.450997	0.340824
O	0.894680	2.322356	-0.391816
C	-1.895525	1.203862	0.669508
H	-1.977967	0.876524	1.709499
H	-0.907339	1.620199	0.432653
H	-2.667268	1.946171	0.455583
S	-2.248075	-0.193096	-0.402736
C	-1.076562	-1.341650	0.329604
H	-1.327853	-1.458012	1.387256
H	-1.202115	-2.293184	-0.189765
H	-0.058456	-0.971694	0.199690
O	-3.638183	-0.700365	-0.028615

Conformer S5e

C	-2.244604	-1.656114	0.241525
C	-2.608505	-0.873885	-0.868478
C	-2.278250	0.480144	-0.939613
C	-1.545613	1.159592	0.099546
C	-1.226004	0.326461	1.232108
C	-1.562568	-1.027155	1.294807
H	-2.506292	-2.709949	0.293524
H	-3.155125	-1.331802	-1.693702
H	-2.559763	1.070138	-1.811124
H	-1.280042	-1.604050	2.175897
H	-0.702660	0.798531	2.062999
O	-1.177721	2.380678	0.012608
C	1.893016	1.421409	-0.100485
H	2.268877	1.589118	-1.113990
H	0.844519	1.732683	-0.003878
H	2.514533	1.969907	0.610410
S	2.108016	-0.320990	0.280295
C	1.092058	-0.963701	-1.056624
H	1.482857	-0.573871	-2.000580
H	1.194386	-2.049727	-1.032206
H	0.049780	-0.681309	-0.899292
O	3.553157	-0.664970	-0.073794

Conformer S5f

C	-1.672881	0.956220	0.863664
C	-1.384183	0.909217	-0.544612
C	-2.076673	-0.133419	-1.253164
C	-2.876204	-1.079196	-0.609955
C	-3.095512	-1.023572	0.775754
C	-2.469762	0.002798	1.500405
H	-1.912806	-0.192239	-2.328961
H	-3.359354	-1.857579	-1.201624
H	-3.711256	-1.766889	1.275711
H	-2.634564	0.080573	2.575654
H	-1.206931	1.752895	1.442526
O	-0.561177	1.710615	-1.117245
C	1.229326	-1.124534	-0.566791
H	0.765939	-1.392435	0.385972
H	0.534935	-0.539499	-1.172955
H	1.557437	-2.021389	-1.095524
S	2.694874	-0.128781	-0.267466
C	1.879427	1.113642	0.737054
H	1.507558	0.625425	1.641584
H	2.630123	1.862912	0.996206
H	1.059900	1.548614	0.144992
O	3.617403	-0.931468	0.642461

Local minimum Me_2SO-4-methylphenolate conformers (Fig. S6)

Conformer S6a

C	1.919076	-0.433241	-1.201635
C	2.518579	-0.825286	0.054952
C	2.166662	0.051757	1.149758
C	1.342395	1.169552	0.993813
C	0.756911	1.501706	-0.241008
C	1.080179	0.672342	-1.332433
H	2.143071	-1.053412	-2.069390
H	0.654193	0.901573	-2.311898
H	1.139971	1.802121	1.862586
H	2.590180	-0.181973	2.126279
O	3.264742	-1.845704	0.186467
C	-0.055053	2.758299	-0.424993
H	0.548911	3.588941	-0.816037
H	-0.882299	2.597466	-1.127566
H	-0.484941	3.093936	0.526822
C	-2.200239	0.468653	1.291989
H	-2.565796	-0.239221	2.041149
H	-1.196977	0.826146	1.529158
H	-2.898036	1.302892	1.200773
S	-2.155113	-0.380848	-0.299149
C	-0.950082	-1.614443	0.201640
H	-1.385538	-2.198146	1.017815
H	-0.756886	-2.256451	-0.658471
H	-0.020240	-1.121281	0.495816
O	-3.499040	-1.087428	-0.434361

Conformer S6b

C	-1.590340	-0.662850	-1.153242
C	-2.327698	-1.052882	0.026941
C	-2.362701	-0.019008	1.039334
C	-1.729786	1.215584	0.889781
C	-0.992701	1.544024	-0.263229
C	-0.961973	0.578431	-1.284119
H	-1.548208	-1.385671	-1.968723
H	-0.421468	0.805224	-2.206722
H	-1.792911	1.944304	1.701734
H	-2.914447	-0.242556	1.952155
O	-2.883613	-2.188009	0.163589
C	-0.342357	2.893422	-0.429996
H	-1.053037	3.661104	-0.767038
H	0.092910	3.244122	0.513772
H	0.466210	2.847044	-1.167885
C	1.946273	-1.472239	-1.008575
H	2.276052	-2.349609	-0.445746
H	0.883525	-1.527787	-1.253808
H	2.549577	-1.363856	-1.911671
S	2.235816	-0.015357	0.013310
C	1.137118	-0.518320	1.341448
H	1.520982	-1.451826	1.763017
H	1.152667	0.269218	2.096145
H	0.120948	-0.630698	0.955150
O	3.663504	-0.138274	0.533486

Conformer S6c

C	1.509432	-0.713431	-1.150121
C	2.225962	-1.134365	0.032022
C	2.396979	-0.070114	0.997081
C	1.849957	1.203555	0.830744
C	1.101759	1.553364	-0.308072
C	0.957099	0.561584	-1.294215
H	1.400690	-1.448930	-1.947869
H	0.416802	0.805466	-2.212034
H	2.010035	1.954277	1.608498
H	2.973573	-0.304003	1.891755
O	2.679153	-2.311625	0.194676
C	0.435489	2.898815	-0.436009
H	-0.580209	2.904049	-0.014050
H	1.009974	3.674923	0.083499
H	0.346253	3.197117	-1.487040
C	-1.154188	-0.234464	1.365026
H	-1.572373	-1.042365	1.972480
H	-0.137693	-0.457663	1.031887
H	-1.155055	0.699112	1.929677
S	-2.222882	-0.006616	-0.060213
C	-1.929165	-1.641359	-0.759107
H	-2.254167	-2.387610	-0.029399
H	-2.533357	-1.721099	-1.664538
H	-0.866384	-1.741986	-0.990498
O	-3.660641	-0.009243	0.446191

Conformer S6d

C	1.031347	-1.078923	1.204008
C	0.517407	-1.672651	0.000122
C	1.031692	-1.079196	-1.203780
C	1.895554	0.017657	-1.196506
C	2.335094	0.607386	0.000055
C	1.895163	0.017987	1.196604
H	0.702692	-1.508913	2.150149
H	2.228975	0.437314	2.148228
H	2.229709	0.436693	-2.148132
H	0.703059	-1.509626	-2.149727
O	-0.361694	-2.609936	0.000067
C	3.292541	1.772685	-0.000044
H	4.342785	1.449370	-0.000265
H	3.144130	2.402884	-0.884127
H	3.144472	2.402777	0.884172
C	-2.145033	-0.222309	1.326342
H	-3.237190	-0.279479	1.281445
H	-1.677964	-1.202479	1.184263
H	-1.833896	0.228544	2.270091
S	-1.608473	0.873954	-0.000046
C	-2.144880	-0.222153	-1.326646
H	-3.237029	-0.279458	-1.281818
H	-1.833729	0.228950	-2.270280
H	-1.677672	-1.202265	-1.184781
O	-2.577816	2.056128	0.000006

Conformer S6e

C	-2.329583	-0.600440	-0.000157
C	-1.891118	-0.010181	-1.196810
C	-1.046051	1.101391	-1.203740
C	-0.521953	1.686597	-0.000092
C	-1.046448	1.101704	1.203469
C	-1.891515	-0.009862	1.196473
H	-2.231984	-0.424307	-2.148173
H	-0.728530	1.540905	-2.149349
H	-2.232701	-0.423796	2.147805
H	-0.729203	1.541341	2.149119
O	0.355358	2.625466	0.000019
C	-3.173270	-1.850518	-0.000198
H	-2.559195	-2.760849	-0.000313
H	-3.818871	-1.890650	0.884953
H	-3.818956	-1.890499	-0.885298
C	2.127169	0.221834	1.327191
H	3.219753	0.271301	1.283473
H	1.666885	1.205188	1.185647
H	1.811865	-0.227343	2.270354
S	1.584824	-0.870208	-0.000333
C	2.128959	0.223842	-1.325422
H	3.221453	0.273782	-1.279765
H	1.815540	-0.224315	-2.269698
H	1.667938	1.206808	-1.183406
O	2.547352	-2.058021	-0.000556

Conformer S6f

C	0.847042	-0.805364	1.228211
C	0.950035	-1.735465	0.132552
C	1.813977	-1.282882	-0.928228
C	2.430098	-0.029614	-0.918642
C	2.266874	0.873241	0.148085
C	1.470352	0.444843	1.222792
H	0.245588	-1.110076	2.084251
H	1.332670	1.108277	2.079224
H	3.059302	0.258001	-1.763970
H	1.958148	-1.957765	-1.771453
O	0.311421	-2.843072	0.097024
C	2.875216	2.252658	0.115564
H	3.056318	2.625906	1.129958
H	3.835046	2.250062	-0.414181
H	2.226561	2.982475	-0.388970
C	-2.430072	-1.124906	-0.095622
H	-2.819458	-1.200563	-1.115026
H	-1.499844	-1.695524	0.024250
H	-3.184524	-1.485622	0.606756
S	-2.192531	0.617947	0.274454
C	-1.060904	0.970720	-1.078354
H	-1.578105	0.742687	-2.014704
H	-0.831430	2.036808	-1.030585
H	-0.147704	0.384850	-0.962935
O	-3.504894	1.317314	-0.073529

Conformer S6g

C	1.487826	-0.449729	-1.208664
C	0.838813	0.787228	-1.223012
C	0.928595	1.730617	-0.137643
C	1.781184	1.292330	0.938252
C	2.421655	0.051401	0.938021
C	2.281873	-0.859829	-0.124976
H	1.359957	-1.123732	-2.058365
H	0.228019	1.071367	-2.079527
H	1.894951	1.967316	1.786046
H	3.041568	-0.224982	1.793936
O	0.275128	2.829957	-0.115259
C	3.012899	-2.178786	-0.135509
H	4.026638	-2.090351	-0.550280
H	3.110411	-2.585147	0.877982
H	2.477240	-2.919218	-0.740445
C	-2.454698	1.105683	0.064489
H	-2.857113	1.196011	1.077633
H	-1.525414	1.678591	-0.052742
H	-3.201997	1.451522	-0.652852
S	-2.205802	-0.641988	-0.273220
C	-1.081509	-0.966196	1.092285
H	-1.600952	-0.715592	2.021594
H	-0.854309	-2.033352	1.069345
H	-0.166314	-0.385297	0.966401
O	-3.517588	-1.341413	0.076926

Conformer S6h

C	-1.256725	-0.879479	1.150604
C	-0.831308	-1.425402	-0.108981
C	-1.581979	-0.939261	-1.234213
C	-2.560080	0.050456	-1.119261
C	-2.916259	0.601784	0.123513
C	-2.234211	0.113673	1.250490
H	-0.761646	-1.247189	2.048916
H	-2.498514	0.499297	2.237504
H	-3.081282	0.387567	-2.017892
H	-1.329625	-1.348324	-2.212521
O	0.141975	-2.256269	-0.223680
C	-3.932727	1.710690	0.233786
H	-3.482083	2.704772	0.109199
H	-4.712471	1.609031	-0.530017
H	-4.423934	1.696849	1.213501
C	2.258489	-0.459981	1.210383
H	1.720470	0.337830	1.728877
H	1.576692	-1.257290	0.877483
H	3.056078	-0.850354	1.845671
S	3.034957	0.247819	-0.243525
C	1.506348	0.708708	-1.068003
H	0.904941	1.332244	-0.401816
H	1.783866	1.266825	-1.964155
H	0.965354	-0.205804	-1.319775
O	3.734719	1.534060	0.180119

Conformer S6i

C	-1.291400	0.868230	1.098063
C	-0.832760	1.331135	-0.182938
C	-1.545112	0.762622	-1.294218
C	-2.605021	-0.132284	-1.135260
C	-3.016288	-0.578784	0.132096
C	-2.350401	-0.031309	1.241339
H	-1.245623	1.083821	-2.291835
H	-3.104250	-0.525617	-2.023384
H	-2.646377	-0.344594	2.244819
H	-0.800135	1.274309	1.981872
O	0.165345	2.128117	-0.326795
C	-4.193518	-1.506982	0.298077
H	-5.144988	-0.963553	0.378946
H	-4.280291	-2.189524	-0.555144
H	-4.089578	-2.117232	1.202583
C	1.643037	-0.761961	-1.052713
H	1.093032	-1.450396	-0.406466
H	1.033623	0.113318	-1.288388
H	1.973157	-1.274836	-1.957991
S	3.120410	-0.201090	-0.197824
C	2.267504	0.448616	1.240330
H	1.758102	-0.380118	1.739029
H	3.024885	0.876286	1.900272
H	1.556368	1.211262	0.888986
O	3.895815	-1.439539	0.237198

Local minimum Me_2SO_2-phenolate conformers (Fig. S7)

Conformer S7a

C	1.983117	0.395914	-1.209906
C	2.376384	-0.943280	-1.197027
C	2.535975	-1.644722	0.009723
C	2.364300	-0.935220	1.210129
C	1.971333	0.404319	1.209651
C	1.818794	1.173622	-0.003666
H	1.878448	0.926615	-2.156204
H	2.518748	-1.464226	-2.144813
H	2.851782	-2.685011	0.014833
H	2.498133	-1.449198	2.162906
H	1.856932	0.941244	2.151277
O	1.514629	2.409712	-0.009262
C	-0.909264	-1.349612	-0.047314
H	-0.326986	-1.209022	-0.957609
H	-0.263368	-1.215959	0.820736
H	-1.397854	-2.325628	-0.033672
C	-1.362260	1.398767	0.013569
H	-0.742329	1.488016	-0.877597
H	-2.138811	2.165665	0.030129
H	-0.727191	1.463913	0.896002
O	-2.983211	-0.255687	-1.248181
S	-2.217179	-0.152831	0.001718
O	-2.931781	-0.302753	1.276888

Conformer S7b

C	-2.875149	-1.452472	0.097591
C	-2.858682	-0.684255	-1.079239
C	-2.291866	0.589841	-1.103217
C	-1.626677	1.164249	0.037078
C	-1.751236	0.385363	1.241949
C	-2.320469	-0.889958	1.258174
H	-3.314140	-2.446740	0.112064
H	-3.313602	-1.081273	-1.987338
H	-1.335221	0.809104	2.155101
H	-2.350664	-1.447532	2.194806
H	-2.271716	1.166130	-2.027760
O	-0.965462	2.259460	-0.021509
C	1.599414	0.876239	1.140215
H	0.868530	1.559894	0.683682
H	1.128460	0.287928	1.926956
H	2.472113	1.410407	1.520775
C	0.774957	-0.715395	-0.997243
H	0.381687	0.172782	-1.490334
H	1.109078	-1.458480	-1.723862
H	0.025644	-1.134691	-0.323070
O	3.110448	0.493198	-0.986353
S	2.221701	-0.248296	-0.082678
O	2.748871	-1.440966	0.596610

Local minimum Me_2SO_2-4-methylphenolate conformers (Fig. S8)

Conformer S8a

C	-1.564463	1.018799	1.208990
C	-2.204221	-0.223325	1.204950
C	-2.531223	-0.888444	0.009947
C	-2.242906	-0.212279	-1.188491
C	-1.605399	1.030203	-1.203639
C	-1.259791	1.747472	0.000262
H	-1.342311	1.514049	2.154247
H	-2.430534	-0.705685	2.158697
H	-2.498203	-0.688221	-2.138326
H	-1.417226	1.535537	-2.151070
O	-0.701945	2.893045	-0.002750
C	-3.167746	-2.255948	0.014338
H	-3.802741	-2.397656	-0.867786
H	-2.423665	-3.064997	0.012796
H	-3.796565	-2.395709	0.901180
C	1.890785	1.271324	0.002840
H	1.348134	1.496692	-0.914690
H	1.244197	1.474569	0.855225
H	2.816171	1.847193	0.062409
C	0.849497	-1.306674	-0.176810
H	0.425986	-1.078003	-1.153964
H	1.099966	-2.365975	-0.090367
H	0.155869	-0.996620	0.606455
O	3.205419	-0.686005	-1.180483
S	2.381270	-0.431000	0.009636
O	2.938202	-0.752783	1.330322

Conformer S8b

C	1.578765	1.021281	-1.206132
C	2.227763	-0.215357	-1.194231
C	2.531974	-0.887051	0.003034
C	2.215897	-0.218081	1.198821
C	1.566358	1.018516	1.206593
C	1.251992	1.745338	-0.000667
H	1.363818	1.515389	-2.153774
H	2.469083	-0.695297	-2.145690
H	2.448303	-0.699514	2.151706
H	1.341438	1.510198	2.153162
O	0.689053	2.888150	-0.002047
C	3.283757	-2.194445	0.005264
H	3.041920	-2.789567	-0.882988
H	4.373001	-2.049640	0.013292
H	3.029431	-2.794029	0.887008
C	-0.863893	-1.329563	-0.049025
H	-0.326905	-1.068922	-0.960957
H	-0.260247	-1.060105	0.818195
H	-1.133397	-2.387464	-0.033879
C	-1.892524	1.258962	0.012811
H	-1.305132	1.477936	-0.878019
H	-2.814740	1.842683	0.028703

H	-1.285787	1.458924	0.894983
O	-3.125118	-0.703527	-1.247425
S	-2.397293	-0.439118	0.001614
O	-3.062012	-0.738663	1.277427

Conformer S8c

C	-1.343475	-0.883916	-1.238989
C	-2.117849	0.279619	-1.227480
C	-2.758483	0.733370	-0.061925
C	-2.602956	-0.055476	1.092663
C	-1.833396	-1.219774	1.094476
C	-1.077095	-1.651606	-0.050985
H	-0.874378	-1.215475	-2.164674
H	-2.248555	0.839299	-2.156110
H	-3.120261	0.239484	2.008236
H	-1.724081	-1.803027	2.008564
O	-0.237960	-2.619451	-0.013085
C	-3.544494	2.020775	-0.040971
H	-3.980283	2.231095	-1.024382
H	-4.366208	1.968733	0.682658
H	-2.923370	2.884704	0.231769
C	2.022893	-0.742131	-1.127046
H	1.437121	-1.552461	-0.668261
H	1.449942	-0.264021	-1.920693
H	2.984561	-1.099477	-1.500398
C	0.902245	0.675986	1.000577
H	0.694161	-0.265006	1.508206
H	1.084023	1.480672	1.715783
H	0.082643	0.926734	0.324464
O	3.430748	-0.046038	0.991689
S	2.410605	0.494761	0.084267
O	2.688545	1.761923	-0.608024

Conformer S8d

C	-1.827048	-1.221879	-1.093801
C	-2.598973	-0.058107	-1.096874
C	-2.755516	0.736498	0.052503
C	-2.114809	0.288821	1.221461
C	-1.339065	-0.872559	1.238406
C	-1.075287	-1.649781	0.054760
H	-1.709343	-1.803405	-2.007883
H	-3.111309	0.235558	-2.015507
H	-2.242556	0.854877	2.146873
H	-0.863731	-1.195099	2.164141
O	-0.234530	-2.616544	0.025122
C	-3.593905	1.990984	0.046369
H	-4.451656	1.912665	0.727018
H	-3.015163	2.871564	0.352088
H	-3.987376	2.187358	-0.956941
C	0.907323	0.674982	-1.001475
H	0.700944	-0.266664	-1.508583
H	0.087362	0.924757	-0.325334
H	1.087023	1.480054	-1.716729
C	2.030020	-0.738016	1.128627

H	1.441503	-1.547990	0.672674
H	2.992219	-1.096497	1.499477
H	1.460446	-0.258109	1.923615
O	3.436837	-0.044252	-0.991482
S	2.415980	0.497174	-0.085196
O	2.692633	1.765857	0.604906

Conformer S8e

C	-2.776591	-0.728218	0.046595
C	-2.607832	0.068004	-1.101023
C	-1.811385	1.213709	-1.095078
C	-1.065984	1.636105	0.060964
C	-1.333157	0.852930	1.238378
C	-2.132859	-0.293006	1.217420
H	-3.117268	-0.218990	-2.023546
H	-0.850493	1.162069	2.164744
H	-2.265348	-0.864271	2.138770
H	-1.679334	1.794487	-2.007753
O	-0.216678	2.595773	0.033876
C	-3.678673	-1.937141	0.043629
H	-3.354300	-2.671745	0.789158
H	-4.721555	-1.677298	0.272312
H	-3.673450	-2.431465	-0.934554
C	2.040766	0.721320	1.140826
H	1.449996	1.533642	0.691452
H	1.471812	0.231761	1.930375
H	3.001349	1.079273	1.516317
C	0.923991	-0.669251	-1.005699
H	0.716388	0.279260	-1.499423
H	1.106542	-1.463648	-1.732040
H	0.104014	-0.930574	-0.333921
O	3.452262	0.053532	-0.984382
S	2.431304	-0.499858	-0.085492
O	2.709556	-1.775740	0.590495