Supplementary Material: Hydrogen bonding networks and cooperativity in the aqueous solvation of trimethylene oxide and sulfide rings by microwave spectroscopy and computational chemistry

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Appendix 1: Cartesian coordinates for the conformers of the studied complexes

Appendix 2: Calculated spectroscopic parameters for the TMO and TMS mono- and dihydrates at the MP2 level

Appendix 3: Fitted parameters and observed transition frequencies for the assigned conformers of TMO–w, TMO–$(w)_2$ and TMS–(w)

Appendix 4: Calculated rotational and centrifugal distortion constants for the observed conformers obtained at the B2PLYP-D3(BJ) level of theory

Appendix 5: Kraitchman analysis for TMO–w and TMS–w

Appendix 6: QTAIM and NCI results for the TMSe mono- and dihydrates

Appendix 1: Cartesian coordinates for the conformers of the studied complexes

Table S1. Cartesian coordinates for the conformer of TMO–w obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.745651	-1.041271	0.072909
C	-0.747335	1.041302	0.071071
C	-1.606771	-0.001324	-0.659145
H	-0.053770	-1.599954	-0.555988
H	-1.265390	-1.718223	0.747918
H	-0.056381	1.600025	-0.558814
H	-1.268182	1.718605	0.744877
H	-1.526030	-0.002219	-1.741176
H	-2.653226	-0.001906	-0.370733
O	2.487831	-0.000146	-0.347932
H	1.710793	0.001040	0.238075
H	3.248924	0.000521	0.236407
O	-0.044871	0.001249	0.813785

Table S2. Cartesian coordinates for the *axial* conformer of TMO–w obtained at the MP2/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	0.791283	1.032157	0.115746
C	0.791301	-1.032146	0.115845
C	1.152533	-0.000046	-0.958486
H	0.071747	1.803883	-0.149443
H	1.650017	1.471121	0.625296
H	0.071778	-1.803911	-0.149271
H	1.650047	-1.471050	0.625428
H	0.450710	-0.000093	-1.787014
H	2.174853	-0.000055	-1.323840
O	-2.318263	-0.000021	-0.302943
H	-1.590292	0.000015	0.343568
H	-3.119996	0.000000	0.226046
O	0.180651	0.000052	0.948423

Table S3. Cartesian coordinates for the *equatorial* conformer of TMO–w obtained at the MP2/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.708975	-1.032744	-0.031189
C	-0.708975	1.032744	-0.031189
C	-1.649656	-0.000000	0.600499
H	-1.149920	-1.801984	-0.661201
H	0.002771	-1.475337	0.667130
H	-1.149920	1.801984	-0.661201
H	0.002771	1.475337	0.667130
H	-2.640409	-0.000000	0.155815
H	-1.723727	-0.000000	1.683362
O	2.467644	0.000000	0.343397
H	1.715839	0.000000	-0.275679
H	3.247861	0.000000	-0.216655
O	-0.059425	-0.000000	-0.832727

Table S4. Cartesian coordinates for the most stable conformer of TMO–$(w)_2$ obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-1.122631	-0.261545	1.024638
C	-1.104711	-0.010727	-1.045500
C	-1.684098	0.828018	0.101240
H	-1.844489	-0.825894	1.611776
H	-0.286413	0.048417	1.647994
H	-1.816255	-0.418020	-1.761290
H	-0.259883	0.441062	-1.560645
H	-2.766495	0.911476	0.102576
H	-1.226934	1.803291	0.221053
O	1.562094	1.631623	0.001267
H	1.932897	0.731138	0.010567
H	2.259035	2.197779	0.339549
O	-0.657214	-1.048041	-0.116609
O	2.056501	-1.122849	0.057396
H	2.489257	-1.678821	-0.594047
H	1.092855	-1.269041	-0.054957

Table S5. Cartesian coordinates for the *axial* conformer of TMS–w obtained at the B2PLYP-D3(BJ) /aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.785074	0.393995	-1.146851
C	-0.785016	0.393995	1.146868
C	-0.562194	1.395480	0.000003
H	-0.079368	0.435556	-1.970011
H	-1.803384	0.378897	-1.526515
H	-0.079267	0.435557	1.969990
H	-1.803307	0.378897	1.526584
H	0.467704	1.742456	-0.000022
H	-1.228121	2.256865	0.000019
S	-0.510497	-1.037103	0.000002
O	2.579887	0.136939	-0.000026
H	1.815448	-0.461107	-0.000052
H	3.349283	-0.437784	0.000121

Table S6. Cartesian coordinates for the *equatorial* conformer of TMS–w obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	0.567717	-0.464757	1.144901
C	0.567717	-0.464757	-1.144901
C	0.999776	-1.396197	0.000000
H	1.252766	-0.364504	1.980329
H	-0.440021	-0.658209	1.501930
H	1.252766	-0.364504	-1.980329
H	-0.440021	-0.658209	-1.501930
H	2.080375	-1.520766	0.000000
H	0.532344	-2.379324	0.000000
S	0.567717	0.995541	0.000000
O	-2.621707	0.280107	0.000000
H	-1.814674	0.818178	0.000000
H	-3.344617	0.912087	0.000000

Table S7. Cartesian coordinates for the *axial* conformer of TMS–$(w)_2$ obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	1.585504	0.077888	-1.074221
C	0.720705	0.974462	0.858130
C	0.793071	1.322953	-0.638280
H	2.659356	0.235549	-1.131375
H	1.238483	-0.434232	-1.965957
H	1.501950	1.432300	1.458979
H	-0.249219	1.102702	1.325256
H	1.267237	2.275403	-0.869335
H	-0.207455	1.317029	-1.062005
O	-1.895882	-1.552788	-0.402163
H	-0.966008	-1.468093	-0.116996
H	-2.243678	-2.302511	0.087771
S	1.157892	-0.795653	0.504204
O	-2.560672	1.124711	0.190384
H	-2.497619	0.180753	-0.036951
H	-3.409665	1.413831	-0.150729

Table S8. Cartesian coordinates for the *equatorial* conformer of TMS–$(w)_2$ obtained at the B2PLYP-D3(BJ)/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	0.981172	0.438059	1.121803
C	0.965701	0.313601	-1.167141
C	1.402820	1.305403	-0.076087
H	-0.017794	0.669295	1.477304
H	1.679289	0.371578	1.949946
H	-0.039024	0.503176	-1.531342
H	1.651108	0.157158	-1.993696
H	0.916312	2.276492	-0.124755
H	2.482438	1.439605	-0.091033
O	-2.289767	-1.241437	-0.079670
H	-2.695421	-1.803115	0.585624
H	-1.330254	-1.407480	-0.010739
S	0.956139	-1.082692	0.056523
O	-1.985111	1.553837	0.054323
H	-2.747886	2.065213	-0.224257
H	-2.269984	0.624103	0.017877

Table S9. Cartesian coordinates for the *axial* conformer of TMSe–w obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.505999	0.844898	-1.176901
C	-0.505760	0.844794	1.177002
C	-0.067925	1.731421	0.000045
H	0.194025	0.757880	-2.000705
H	-1.505274	1.055446	-1.546814
H	0.194435	0.757699	2.000652
H	-1.504959	1.055309	1.547138
H	1.015057	1.834751	-0.000059
H	-0.509087	2.729385	0.000134
O	2.798516	-0.120058	-0.000016
H	1.940425	-0.577137	-0.000101
H	3.459352	-0.818090	-0.000447
Se	-0.564529	-0.775337	-0.000016

Table S10. Cartesian coordinates for the *equatorial* conformer of TMSe–w obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.522404	0.740292	-1.175076
C	-0.522362	0.740302	1.175076
C	-1.056496	1.573746	0.000005
H	0.457815	1.051611	-1.522419
H	-1.196764	0.588752	-2.011033
H	0.457867	1.051627	1.522387
H	-1.196696	0.588767	2.011055
H	-0.727093	2.613739	-0.000006
H	-2.145654	1.561911	0.000026
O	2.772679	0.500310	-0.000022
H	2.086955	-0.188121	-0.000022
H	3.608919	0.026571	0.000051
Se	-0.321153	-0.871276	0.000003

Table S11. Cartesian coordinates for the *axial* conformer of TMSe–$(w)_2$ obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.128531	1.252610	-0.840776
C	-1.014798	0.818379	1.301034
C	0.002170	1.740559	0.609985
H	0.804397	1.112204	-1.373684
H	-0.844044	1.808525	-1.439435
H	-0.707774	0.375050	2.242312
H	-2.012085	1.239326	1.390086
H	1.009332	1.535158	0.965860
H	-0.194812	2.805213	0.745034
O	3.152757	0.719450	-0.450778
H	2.918056	-0.136899	-0.047893
H	4.053808	0.900107	-0.172227
Se	-0.980642	-0.461438	-0.239461
O	2.071909	-1.633842	0.656266
H	2.258126	-2.487801	0.254993
H	1.144361	-1.432029	0.418795

Table S12. Cartesian coordinates for the *equatorial* conformer of TMSe–$(w)_2$ obtained at the B3LYP-D3(BJ)/aug-cc-pVTZ level of theory.

	Cartesian Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.381296	-0.946225	1.201861
C	-0.383891	-1.019693	-1.146147
C	-0.487006	-1.966474	0.058765
H	0.637646	-0.784737	1.536094
H	-1.053367	-1.079760	2.042723
H	0.634183	-0.882326	-1.493328
H	-1.059130	-1.206145	-1.974384
H	0.285274	-2.734574	0.081306
H	-1.463472	-2.449354	0.075212
O	2.248739	1.687703	0.089085
H	1.279274	1.563322	0.045484
H	2.462256	2.300702	-0.620320
Se	-0.924354	0.549321	-0.019257
O	2.794537	-1.061717	-0.071307
H	2.765674	-0.088152	-0.020825
H	3.678456	-1.310445	0.209824

Appendix 2: Calculated spectroscopic parameters for the TMO and TMS mono- and dihydrates at the MP2 level

Table S13. Calculated relative energies and spectroscopic parameters for the conformers of the mono- and dihydrated complexes of TMO and TMS obtained at the MP2 level of theory

	TMO–w		TMO–$(w)_2$	TMS–w		TMS–$(w)_2$	
Parameter[a]	*axial*	*equatorial*		*axial*	*equatorial*	*axial*	*equatorial*
A/MHz	7253/7371[b]	8618/8615	3558/3511	4437/4454	4688/4710	2851/2810	2698/2698
B/MHz	2913/2804	2652/2583	2067/2015	2526/2464	2394/2335	1481/1453	1687/1620
C/MHz	2859/2737	2465/2405	1620/1577	2225/2179	2172/2127	1229/1188	1266/1226
$\lvert\mu_a\rvert$/D	1.6/1.6	2.0/1.9	0.5/0.4	0.7/0.7	0.5/0.4	0.0/0.0	0.5/0.6
$\lvert\mu_b\rvert$/D	0.0/0.0	0.0/0.0	0.2/0.1	0.3/0.1	0.3/0.1	0.3/0.5	0.2/0.0
$\lvert\mu_c\rvert$/D	0.0/0.3	0.3/0.5	0.4/0.4	0.0/0.0	0.0/0.0	0.6/0.6	0.5/0.5
Complexation energy/kJ mol^{-1}	-29.1/-26.1	-28.9/-25.9	-66.9/-62.8	-23.2/-20.2	-22.8/-19.8	-54.7/-51.0	-56.8/-52.9
ΔE_{ZPE}/kJ mol^{-1}	0.0/0.0	0.2/0.2		0.0/0.0	0.5/0.4	1.5/1.5	0.0/0.0

[a]Rotational constants (*A*, *B* and *C*), absolute electric dipole moment components ($\lvert\mu_a\rvert$, $\lvert\mu_b\rvert$ and $\lvert\mu_c\rvert$), complexation energies accounting for basis set superposition errors and relative ZPE-corrected electronic (ΔE_{ZPE}) energies, [b]aug-cc-pVTZ/def2-TZVP basis set.

Appendix 3: Fitted parameters and observed transition frequencies for the assigned conformers of TMO–w, TMO–$(w)_2$ and TMS–(w)

Table S14. Spectroscopic parameters for the assigned species of TMO–w

Parameter[a]	Parent	^{18}O	C_α (equivalent)	C_β
A/MHz	8097.89(99)	8069.52(85)	7974.10(99)	8016.70(68)
B/MHz	2635.78669(99)	2478.6300(12)	2628.34996(42)	2597.2756(17)
C/MHz	2488.11083(75)	2350.0202(12)	2468.67065(50)	2460.4851(49)
D_J/kHz	20.716(26)	18.778(16)	[20.716][b]	[20.716]
D_{JK}/kHz	-69.10(14)	-63.939(68)	[-69.10]	[-69.10]
d_1/kHz	2.433(23)	2.034(22)	[2.433]	[2.433]
d_2/kHz	-0.070(16)	-0.042(10)	[-0.070]	[-0.070]
N	10	14	5	4
σ/kHz	0.9	2.1	1.1	2.1
$\mu_a/\mu_b/\mu_c$	y/n/n	y/n/n	y/n/n	y/n/n
P_{aa}/amu Å^2	166.23	178.17	166.82	168.48
P_{bb}/amu Å^2	36.89	36.90	37.91	36.93
P_{cc}/amu Å^2	25.51	25.74	25.47	26.11

[a]Rotational constants (*A*, *B* and *C*), quartic centrifugal distortion constants (D_J, D_{JK}, d_1, d_2), number of fitted transitions (*N*), standard deviation of the fit (σ); electric dipole moment components $\mu_a/\mu_b/\mu_c$ "y" if transitions related to the dipole was observed and "n" if not observed; planar moments of inertia (P_{aa}, P_{bb} and P_{cc}). [b]Values in brackets [ ] were fixed to the value determined for the corresponding parent species. The fitting was done using the transition frequencies from the BF-FTMW measurements.

Table S15. Observed transitions for the assigned species of TMO–w

Parent							
J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs} /MHz	$\nu_{obs-calc}$ /MHz
2	1	2	1	1	1	10099.6567	0.0019
2	0	2	1	0	1	10244.1758	0.0000
2	1	1	1	1	0	10395.1627	0.0004
3	1	3	2	1	2	15146.2608	-0.0015
3	0	3	2	0	2	15357.6265	-0.0010
3	2	2	2	2	1	15371.1202	0.0000
3	2	1	2	2	0	15382.9344	-0.0001
3	1	2	2	1	1	15589.7787	0.0000
4	1	4	3	1	3	20189.0504	0.0004
4	0	4	3	0	3	20460.7325	0.0003
^{18}O							
2	1	2	1	1	1	9528.2840	0.0036
2	0	2	1	0	1	9654.5053	0.0006
2	1	1	1	1	0	9785.6330	0.0027
3	1	3	2	1	2	14289.8079	-0.0025
3	0	3	2	0	2	14475.1378	-0.0017
3	2	2	2	2	1	14485.4598	-0.0014
3	2	1	2	2	0	14494.2356	-0.0006
3	1	2	2	1	1	14676.0544	-0.0017
4	1	4	3	1	3	19048.2391	0.0032
4	0	4	3	0	3	19287.8357	-0.0018
4	2	3	3	2	2	19310.1382	-0.0015
4	3	2	3	3	1	19318.7277	0.0014
4	2	2	3	2	1	19332.0740	-0.0017
4	1	3	3	1	2	19563.5796	0.0029
^{13}C' (equivalent)							
2	0	2	1	0	1	10189.8506	-0.0013
2	1	1	1	1	0	10353.4102	-0.0016
3	1	3	2	1	2	15047.276	0.0004
3	0	3	2	0	2	15274.719	0.0000
3	1	2	2	1	1	15526.7921	0.0015
^{13}C"							
2	0	2	1	0	1	10112.2987	-0.0008
2	1	1	1	1	0	10252.0067	0.0034
3	0	3	2	0	2	15160.8056	0.0005
3	1	2	2	1	1	15375.2899	-0.0023

Table S16. Observed transitions for the parent and ^{18}O species of TMO–$(w)_2$

Parent							
J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs} /MHz	$\nu_{obs-calc}$ /MHz
3	1	3	2	1	2	10051.5446	0.0020
3	0	3	2	0	2	10441.2304	0.0010
3	2	2	2	2	1	10764.1386	-0.0047
3	1	2	2	1	1	11368.2530	0.0018
4	1	4	3	1	3	13323.3983	0.0003
4	0	4	3	0	3	13638.6714	-0.0007
4	2	3	3	2	2	14284.7769	0.0012
5	0	5	4	0	4	16753.8877	-0.0014
5	2	4	4	2	3	17750.0089	-0.0011
5	3	3	4	3	2	18139.6204	0.0014
5	1	4	4	1	3	18559.0769	0.0007
5	2	3	4	2	2	18927.8011	-0.0010
6	1	6	5	1	5	19746.2074	0.0006
^{18}O							
3	1	3	2	1	2	9466.6138	0.0012
3	0	3	2	0	2	9843.2069	0.0000
3	2	2	2	2	1	10177.2621	0.0031
3	1	2	2	1	1	10774.8785	0.0002
4	1	4	3	1	3	12541.2820	-0.0005
4	0	4	3	0	3	12837.9823	-0.0005
4	2	3	3	2	2	13499.5665	-0.0019
4	2	2	3	2	1	14230.2417	-0.0017
4	1	3	3	1	2	14233.6744	-0.0002
5	1	5	4	1	4	15572.3827	0.0035
5	0	5	4	0	4	15756.7053	-0.0043
5	2	4	4	2	3	16764.4941	-0.0022
5	3	3	4	3	2	17165.8526	0.0008
5	1	4	4	1	3	17550.7457	0.0027
5	2	3	4	2	2	17960.1496	-0.0003
6	1	6	5	1	5	18569.9675	0.0007

Table S17. Observed transitions for the parent and ^{18}O species of TMS–w

Parent							
J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{obs} /MHz	$\nu_{obs-calc}$ /MHz
2	1	2	1	1	1	9059.3097	-0.0003
2	0	2	1	0	1	9311.5620	0.0007
2	1	1	1	1	0	9619.3400	0.0000
2	1	2	1	0	1	11012.2352	-0.0005
3	1	3	2	1	2	13571.9783	-0.0033
3	0	3	2	0	2	13898.8183	0.0023
3	2	2	2	2	1	14007.5405	0.0015
3	2	1	2	2	0	14117.8463	0.0012
3	1	2	2	1	1	14410.1890	-0.0016
4	1	4	3	1	3	18066.6251	-0.0039
4	0	4	3	0	3	18413.4193	0.0055
4	1	3	3	1	2	19175.9318	-0.0016
^{18}O							
2	1	2	1	1	1	8548.2130	0.0005
2	0	2	1	0	1	8776.4992	0.0000
2	1	1	1	1	0	9045.9253	-0.0016
3	1	3	2	1	2	12809.5672	-0.0004
3	0	3	2	0	2	13113.4011	-0.0002
3	1	2	2	1	1	13554.9883	0.0020
4	1	4	3	1	3	17057.0956	0.0001
4	0	4	3	0	3	17393.8465	0.0000
4	2	2	3	2	1	17775.5280	0.0000
4	1	3	3	1	2	18045.7952	-0.0006

Appendix 4: Calculated rotational and centrifugal distortion constants for the observed conformers obtained at the B2PLYP-D3(BJ) level of theory

Table S18. Calculated parameters for the assigned conformers of TMO–w, TMO–$(w)_2$ and TMS–w

Parameter[a]	TMO–w	TMO–$(w)_2$	TMS–w
A/MHz	8414/8151[b]	3559/3522	4389/4401
B/MHz	2624/2628	2042/2027	2522/2514
C/MHz	2444/2470	1608/1589	2223/2219
D_J/kHz	13.2/18.19	1.67/1.65	5.05/4.85
D_{JK}/kHz	-49.7/-67.58	10.95/15.09	51.30/54.21
d_1/kHz	1.15/2.10	-0.38/-0.36	-0.63/-0.56
d_2/kHz	-0.04/-0.07	-0.03/-0.04	0.45/0.46

[a]Rotational constants (*A*, *B* and *C*) and quartic centrifugal distortion constants (D_J, D_{JK}, d_1, d_2); [b]aug-cc-pVTZ/def2-TZVP basis set.

Appendix 5: Kraitchman analysis for TMO–w and TMS–w

Table S19. Kraitchman substituted atomic coordinates (Å) for the water oxygen in TMO–w and TMS–w

O atom - coordinate	|*a*|		|*b*|		|*c*|	
	Exp.	Calc.[a]	Exp.	Calc.	Exp.	Calc.
TMO–H_2O	2.4704(8)	2.48	0.00[b]	0.00	0.350(6)	-0.35
TMS–H_2O	2.6024(6)	2.58	0.13(1)	0.14	0.00	0.00

[a]B2PLYP-D3(BJ)/aug-cc-pVTZ; [b]Imaginary values were set to zero.

Table S20. Kraitchman coordinates (Å) for the center of mass (COM) of water relative to the principal axis system of the TMO and TMS monomers

	COM water		
Coordinate	|*a*|	|*b*|	|*c*|
TMO	1.951(3)	0.00	2.6967(6)
TMS	0.00[a]	0.00	3.2697(5)

[a]Imaginary values were set to zero.

Appendix 6: QTAIM and NCI results for the TMSe mono- and dihydrates

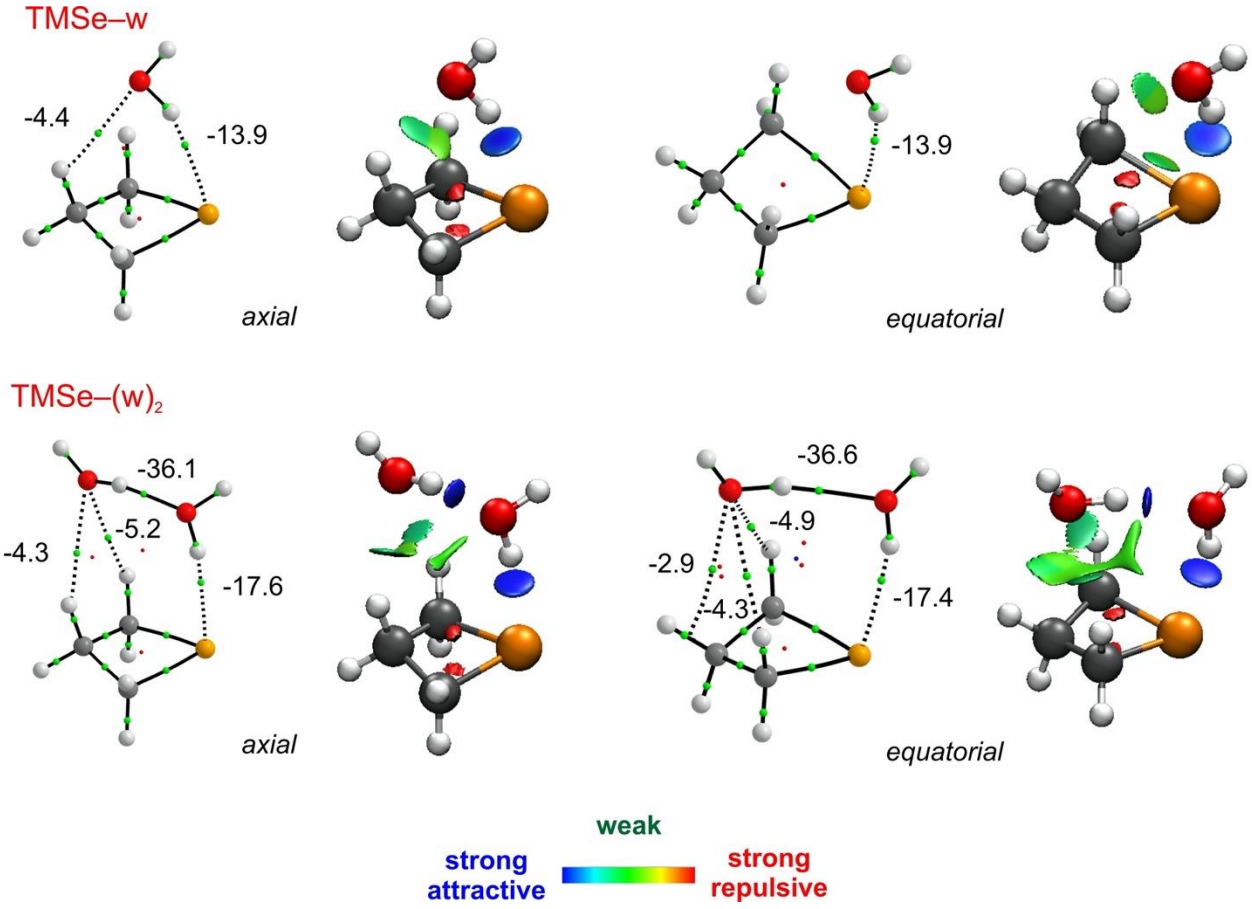

Figure S1. QTAIM molecular graphs (left) and NCI isosurfaces (right, *s*= 0.5, colour scale BGR -0.02 < ρ < +0.02) for the conformers of the TMSe–(w) and TMSe–$(w)_2$