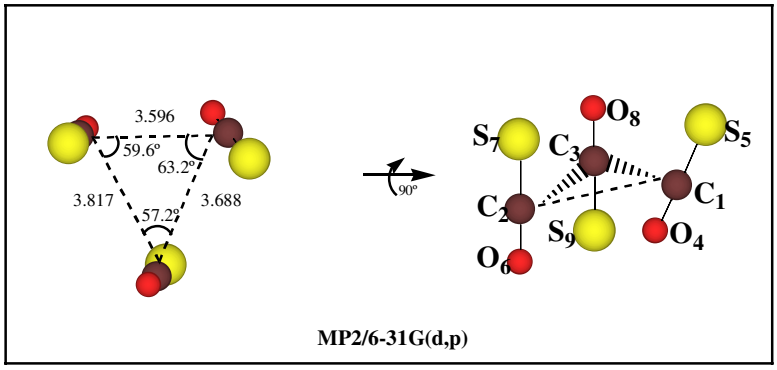
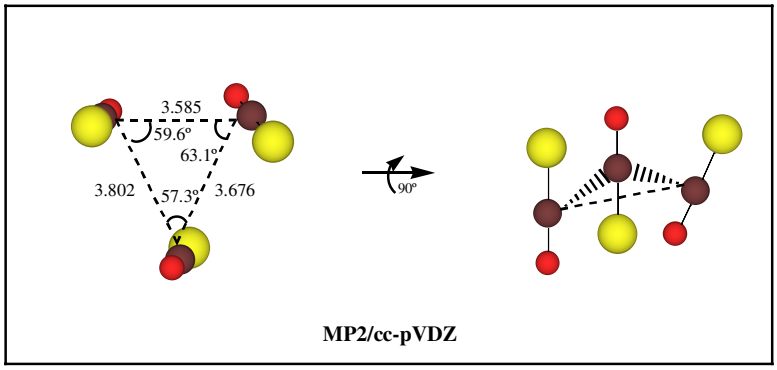
Supporting

Information

Figure S1. Geometrical parameters calculated at different levels of theory for MI.





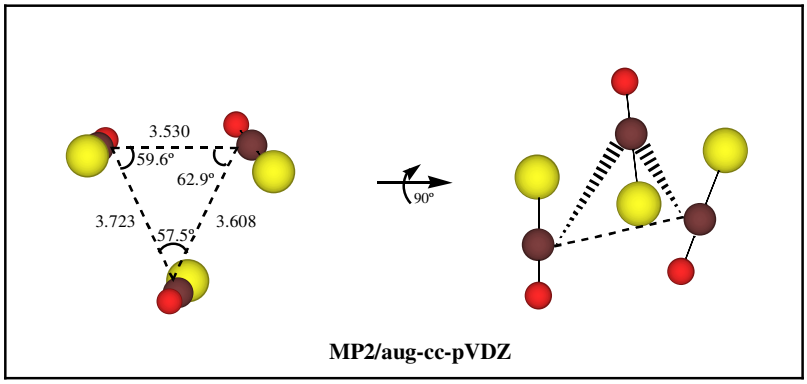
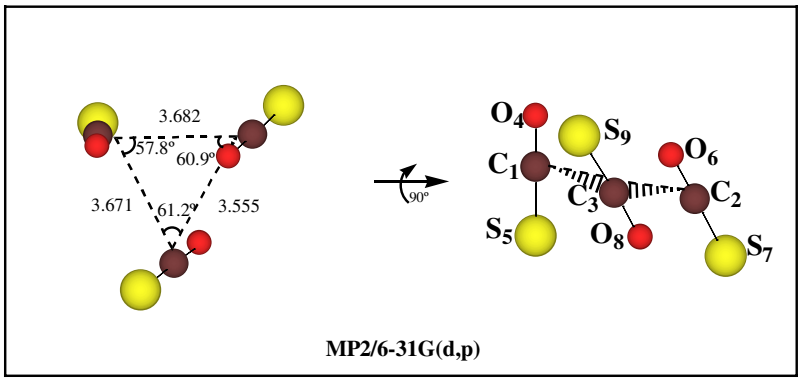
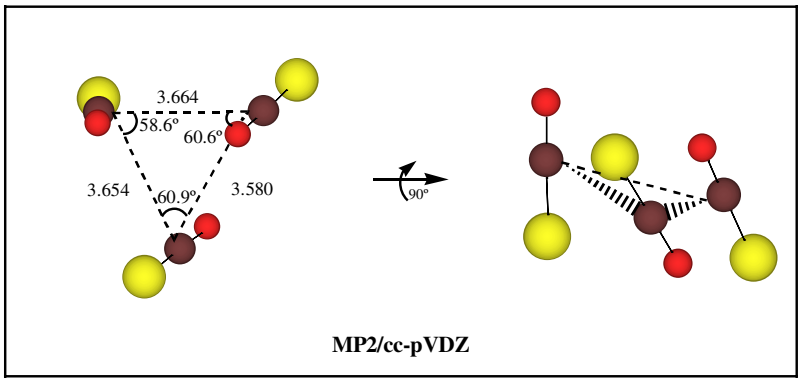


Figure S1 (cont.). Geometrical parameters calculated at different levels of theory for MII.





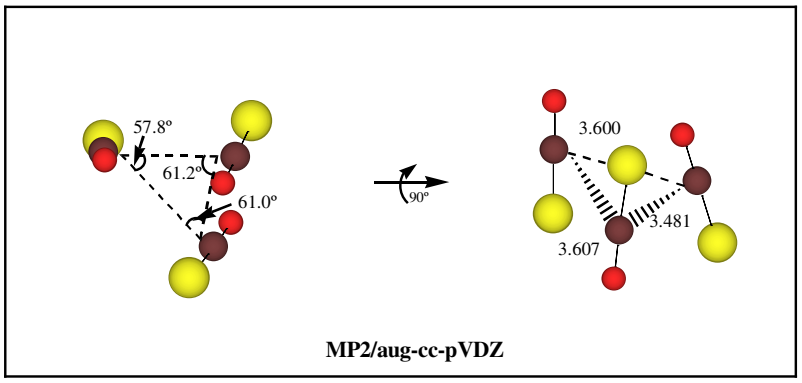
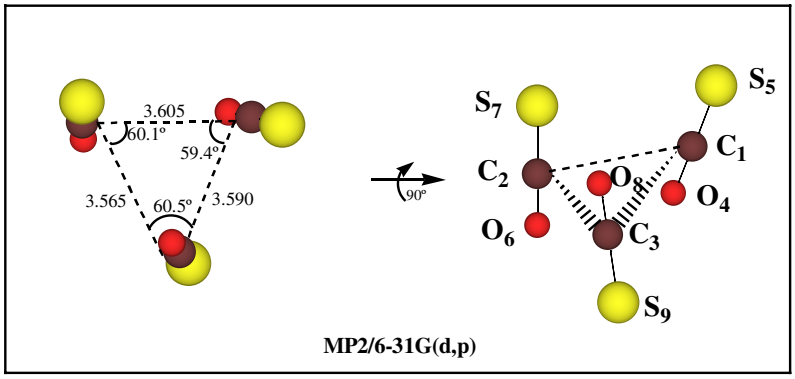
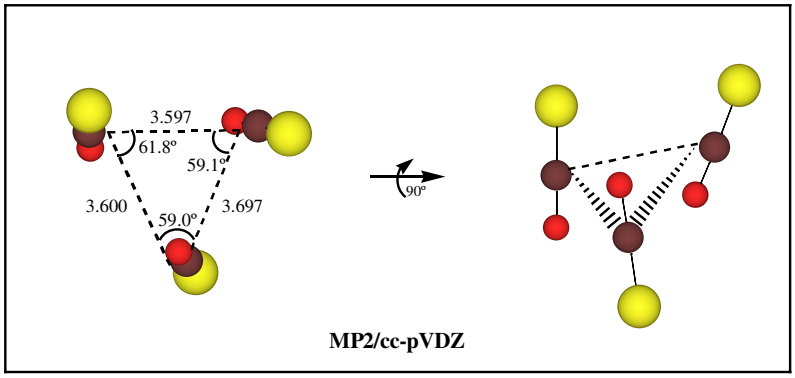


Figure S1 (cont.). Geometrical parameters calculated at different levels of theory for MIII.





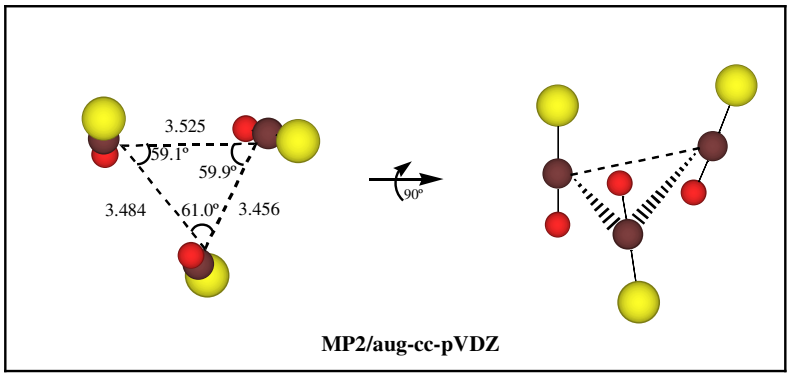


Figure S1 (cont.). Geometrical parameters calculated at different levels of theory for MIV.

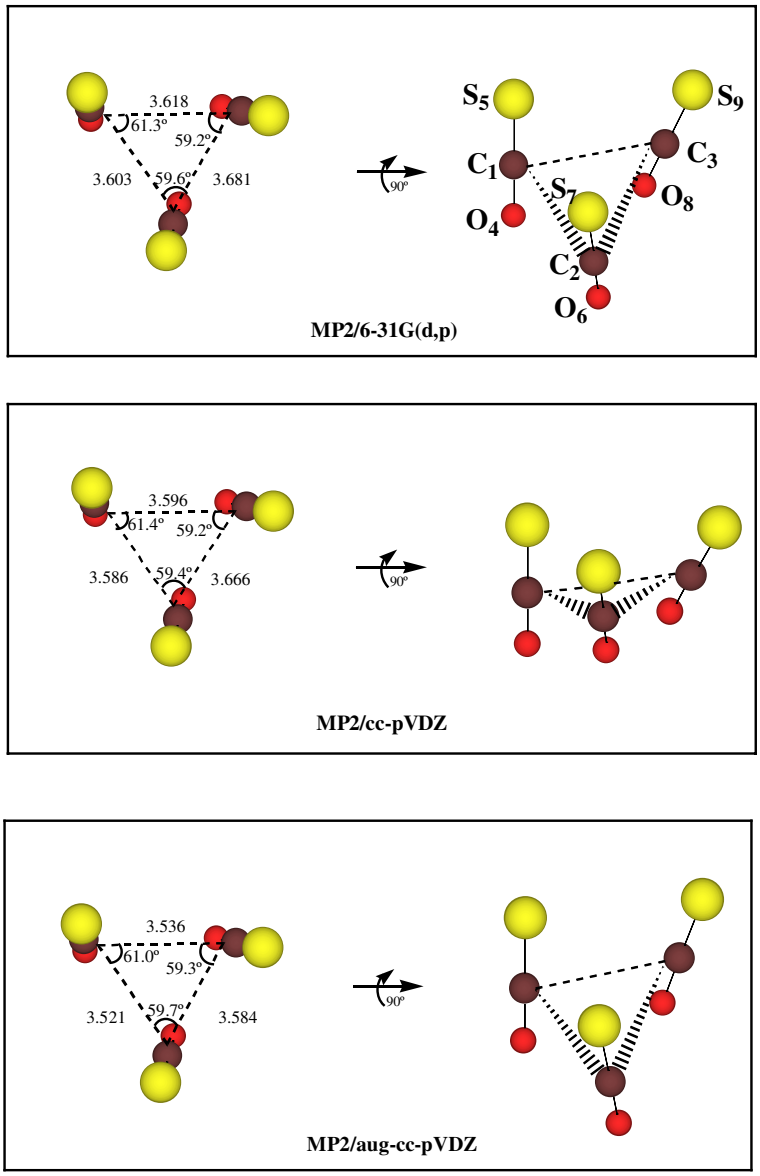


Figure S1 (cont.). Geometrical parameters calculated at different levels of theory for MV.

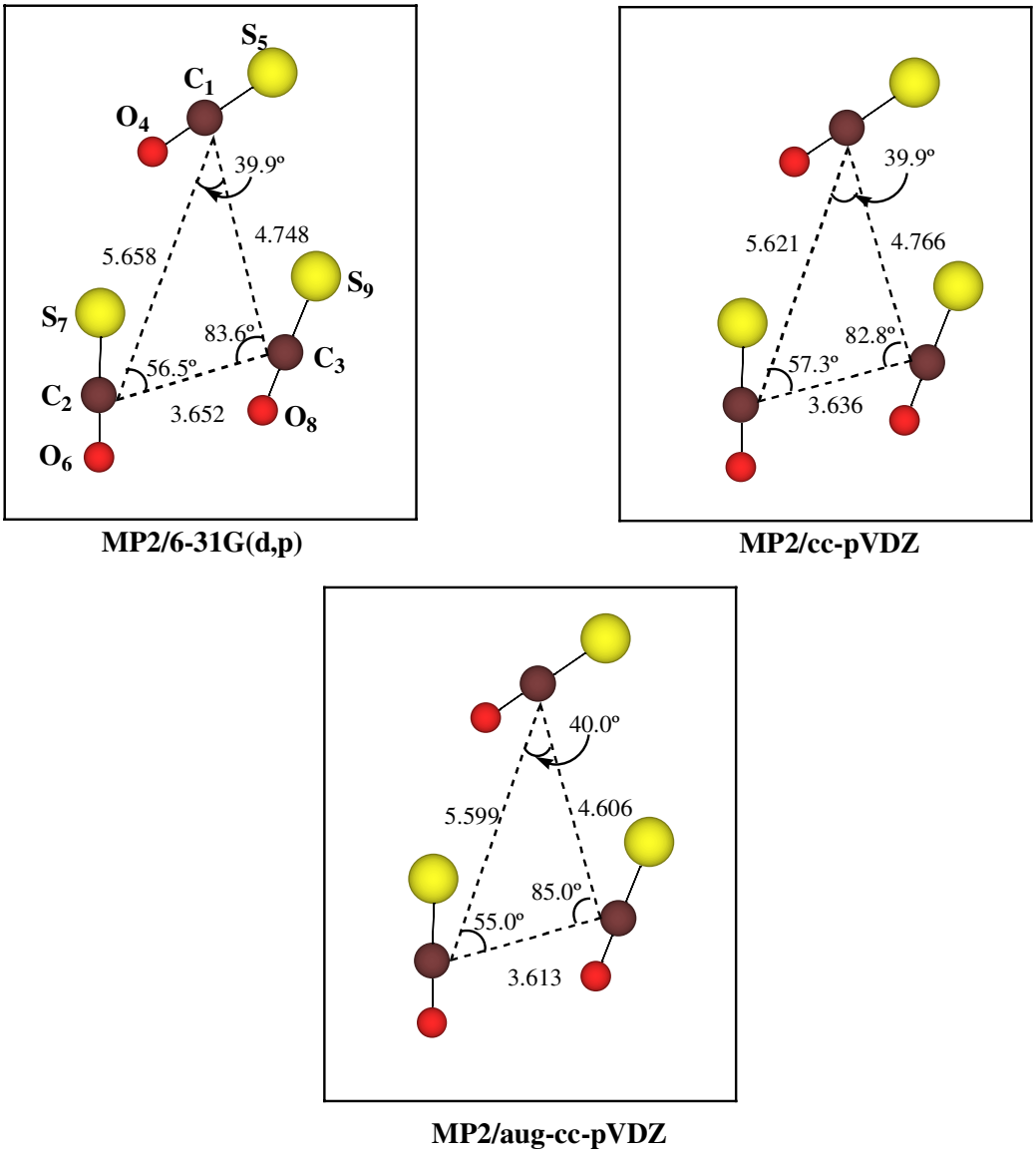


Figure S1 (cont.). Geometrical parameters calculated at different levels of theory for MVI.

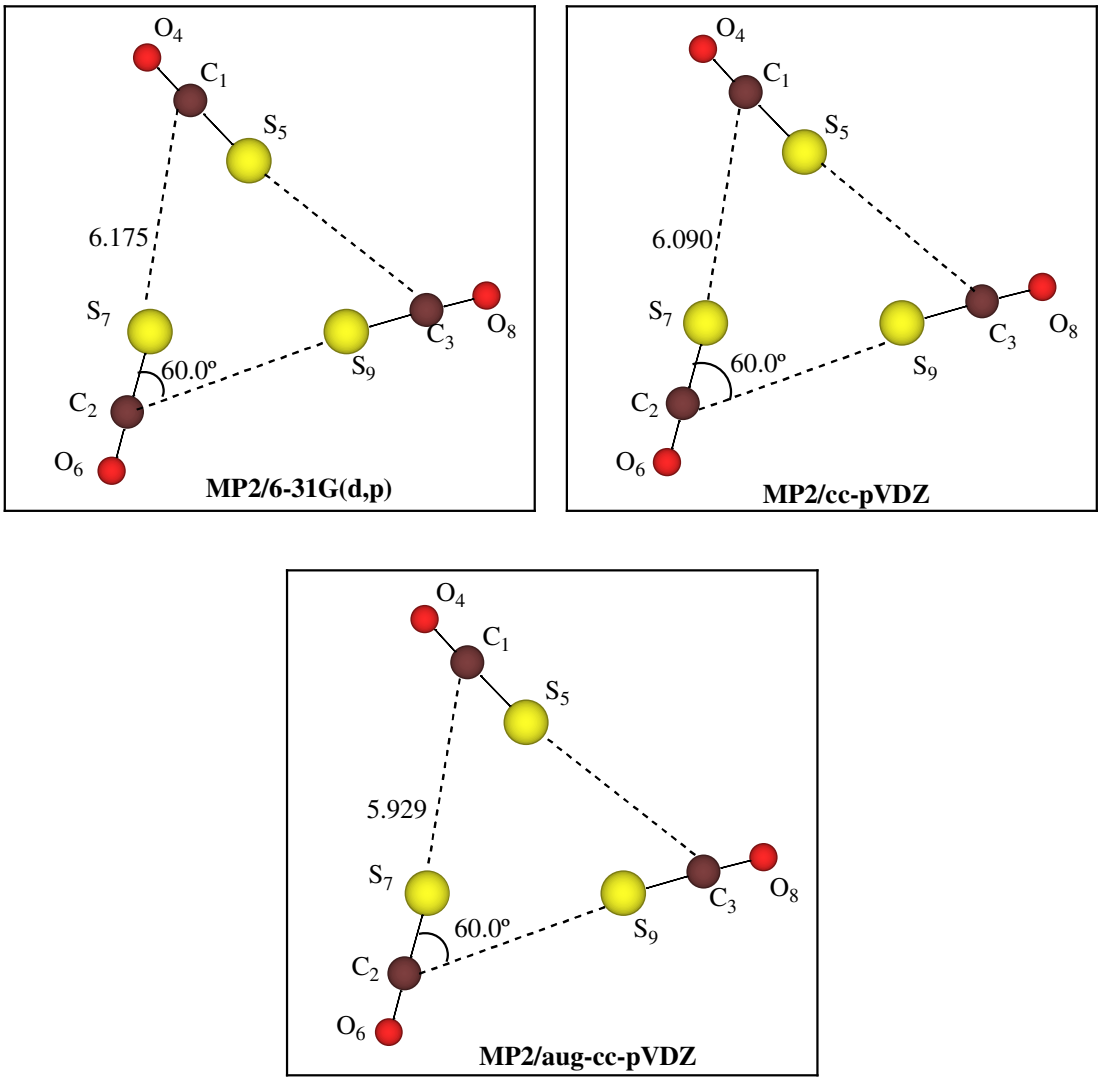


Table S1. Most representative geometrical parameters for the minima structures localized on the potential energy surface of $(OCS)_3$. Distances are given in Å and angles in degrees.

Parameters	Exptl.[a]	MI			MII		
		6-31G(d,p)	cc-pVDZ	aug-cc-pVDZ	6-31G(d,p)	cc-pVDZ	aug-cc-pVDZ
r(C_1-C_2)	3.654	3.596	3.585	3.530	3.682	3.664	3.600
r(C_1-C_3)	3.797	3.688	3.676	3.608	3.671	3.654	3.607
r(C_2-C_3)	3.908	3.817	3.802	3.723	3.555	3.580	3.481
(C_1-C_2-C_3)	60.2	59.6	59.6	59.6	60.9	60.6	61.2
(C_2-C_3-C_1)	56.6	57.2	57.3	57.5	61.2	60.9	61.0
(C_3-C_1-C_2)	63.2	63.2	63.1	62.9	57.8	58.6	57.8
(S_5-C_1-C_3)	70.9	79.4	78.8	75.8	81.3	80.2	75.9
(S_7-C_2-C_1)	82.8	81.8	81.5	77.8	127.4	124.9	123.0
(O_8-C_3-C_2)	116.5	108.0	108.1	110.2	60.6	61.2	68.9
(S_5-C_1-C_3-C_2)	136.4	134.8	132.7	135.0	82.5	81.3	80.1
(S_7-C_2-C_1-C_3)	80.0	75.3	75.3	74.5	106.7	106.6	105.3
(O_8-C_3-C_2-C_1)	89.9	91.5	92.8	95.0	122.3	123.7	125.9
(S_5-C_1-C_3-S_9)	-156.2	-149.9	-151.2	-149.9	-145.9	-146.7	-148.7
(S_7-C_2-C_1-S_5)	32.7	19.7	18.7	22.2	20.2	20.5	22.2
(S_9-C_3-C_2-S_7)	-178.8	-178.6	-177.2	-172.1	-176.5	-172.4	-168.9

[a] See Ref. 6.

Table S1 (cont).

Parameters	Exptl.[a]	MIII			MIV		
		6-31G(d,p)	cc-pVDZ	aug-cc-pVDZ	6-31G(d,p)	cc-pVDZ	aug-cc-pVDZ
r(C_1-C_2)	3.654	3.605	3.597	3.525	3.603	3.586	3.521
r(C_1-C_3)	3.797	3.590	3.697	3.456	3.618	3.596	3.536
r(C_2-C_3)	3.908	3.565	3.600	3.484	3.681	3.666	3.584
(C_1-C_2-C_3)	60.2	60.1	61.8	59.1	59.6	59.4	59.7
(C_2-C_3-C_1)	56.6	60.5	59.0	61.0	59.2	59.2	59.3
(C_3-C_1-C_2)	63.2	59.4	59.1	59.9	61.3	61.4	61.0
(S_5-C_1-C_3)	70.9	120.2	123.5	115.8	82.1	81.7	77.9
(S_7-C_2-C_1)	82.8	82.3	81.2	78.3	83.8	82.9	78.8
(O_8-C_3-C_2)	116.5	61.0	60.8	62.6	51.9	54.4	56.2
(S_5-C_1-C_3-C_2)	136.4	112.6	109.4	112.1	135.8	132.5	135.0
(S_7-C_2-C_1-C_3)	80.0	132.4	131.7	131.3	82.5	80.8	79.7
(O_8-C_3-C_2-C_1)	89.9	70.0	68.7	74.9	-69.0	-71.6	-70.9
(S_5-C_1-C_3-S_9)	-156.2	-138.6	-142.9	-139.1	18.2	16.8	21.7
(S_7-C_2-C_1-S_5)	32.7	24.1	18.8	27.4	26.2	22.2	26.5
(S_9-C_3-C_2-S_7)	-178.8	-168.4	-170.2	-160.5	22.4	20.0	23.8

[a] See Ref. 6.

Table S1 (cont).

Parameters	Exptl.[a]	MV			MVI		
		6-31G(d,p)	cc-pVDZ	aug-cc-pVDZ	6-31G(d,p)	cc-pVDZ	aug-cc-pVDZ
r(C_1-C_2)	3.654	5.658	5.621	5.599	6.175	6.090	5.929
r(C_1-C_3)	3.797	4.748	4.766	4.606	6.175	6.090	5.929
r(C_2-C_3)	3.908	3.652	3.636	3.613	6.175	6.090	5.929
(C_1-C_2-C_3)	60.2	56.5	57.3	55.0	60.0º	60.0º	60.0º
(C_2-C_3-C_1)	56.6	83.6	82.8	85.0	60.0º	60.0º	60.0º
(C_3-C_1-C_2)	63.2	39.9	39.9	40.0	60.0º	60.0º	60.0º
(S_5-C_1-C_3)	70.9	103.9	101.3	103.7	7.1	6.0	5.8
(S_7-C_2-C_1)	82.8	20.4	19.3	17.9	7.1	6.0	5.8
(O_8-C_3-C_2)	116.5	55.2	57.5	57.6	172.9	174.0	174.3
(S_5-C_1-C_3-C_2)	136.4	180.0	180.0	180.0	0.0	0.0	0.0
(S_7-C_2-C_1-C_3)	80.0	0.0	0.0	0.0	0.0	0.0	0.0
(O_8-C_3-C_2-C_1)	89.9	180.0	180.0	180.0	180.0	180.0	180.0
(S_5-C_1-C_3-S_9)	-156.2	0.0	0.0	0.0	0.0	0.0	0.0
(S_7-C_2-C_1-S_5)	32.7	180.0	180.0	180.0	0.0	0.0	0.0
(S_9-C_3-C_2-S_7)	-178.8	0.0	0.0	0.0	0.0	0.0	0.0

[a] See Ref. 6.

Table S2. Rotational constants (MHz) and dipole moments (Debye) for the minima structures localized on the potential energy surface of $(OCS)_3$.

Structure	A	B	C	
MI				
6-31G(d,p)	846.5	738.9	588.2	0.517
cc-pVDZ	843.2	741.7	595.3	0.402
aug-cc-pVDZ	889.8	765.8	625.5	0.636
MII				
6-31G(d,p)	959.7	647.2	490.4	0.486
cc-pVDZ	976.2	642.4	493.2	0.381
aug-cc-pVDZ	1017.5	669.8	520.3	0.625
MIII				
6-31G(d,p)	926.4	642.2	434.9	0.552
cc-pVDZ	952.2	607.1	423.2	0.426
aug-cc-pVDZ	959.9	676.5	463.4	0.683
MIV				
6-31G(d,p)	839.9	720.1	507.0	1.401
cc-pVDZ	847.6	726.4	519.3	1.098
aug-cc-pVDZ	891.9	755.4	541.3	1.736
MV				
6-31G(d,p)	1247.5	430.9	320.3	1.628
cc-pVDZ	1247.5	437.6	324.0	1.239
aug-cc-pVDZ	1359.8	439.4	332.1	1.955
MVI				
6-31G(d,p)	512.3	512.3	256.1	0.0
cc-pVDZ	527.0	527.0	263.5	0.0
aug-cc-pVDZ	555.6	555.6	277.8	0.0
Exptl.[a]	847.97958(2)	736.17579(2)	574.32591(1)	0.653(8)

[a] See Refs. 4 and 6.

Table S3. Bond properties (a. u.) for the minima structures located on the PES of the $(OCS)_3$. Atom numbering corresponds to that in Figure S1.

Level	MI				MII				MIII			
	Critical Points	**(r_c)**	**$^2(r_c)$**	**$H(r_c)$**	**Critical Points**	**(r_c)**	**$^2(r_c)$**	**$H(r_c)$**	**Critical Points**	**(r_c)**	**$^2(r_c)$**	**$H(r_c)$**
MP2/6-31G(d,p)	$O_4\cdots O_6$	0.0060	0.0250	0.0010	$O_6\cdots O_8$	0.0061	0.0254	0.0009	$C_2\cdot\cdot O_4$	0.0059	0.0246	0.0010
	$S_5\cdots O_8$	0.0038	0.0131	0.0008	$C_1\cdots O_6$	0.0061	0.0242	0.0010	$O_6\cdots O_8$	0.0062	0.0258	0.0009
	$C_3\cdots S_7$	0.0041	0.0128	0.0007	$O_4\cdots S_9$	0.0038	0.0137	0.0008	$O_4\cdots O_8$	0.0068	0.0271	0.0008
	Ring	0.0022	0.0087	0.0005	Ring	0.0023	0.0091	0.0005	Ring	0.0029	0.0160	0.0010
MP2/cc-pVDZ	$C_2\cdots O_4$	0.0055	0.0228	0.0011	$O_6\cdots O_8$	0.0056	0.0232	0.0009	$C_2\cdot\cdot O_4$	0.0055	0.0229	0.0011
	$C_3\cdots S_5$	0.0042	0.0129	0.0006	$C_1\cdots O_6$	0.0057	0.0214	0.0010	$O_6\cdots O_8$	0.0057	0.0236	0.0009
	$C_3\cdots S_7$	0.0045	0.0122	0.0005	$O_4\cdots S_9$	0.0043	0.0138	0.0007	$O_4\cdots O_8$	0.0064	0.0253	0.0008
	Ring	0.0023	0.0088	0.0005	Ring	0.0024	0.0095	0.0005	Ring	0.0028	0.0144	0.0009
MP2/aug-cc-pVDZ	$C_2\cdots O_4$	0.0061	0.0226	0.0010	$O_6\cdots O_8$	0.0061	0.0258	0.0011	$C_2\cdot\cdot O_4$	0.0063	0.0239	0.0010
	-[a]	-	-	-	$C_1\cdots C_3$	0.0055	0.0134	0.0004	$O_6\cdots O_8$	0.0063	0.0262	0.0011
	$C_2\cdots S_9$	0.0061	0.0144	0.0004	$C_1\cdots O_6$	0.0066	0.0214	0.0007	$O_4\cdots O_8$	0.0065	0.0268	0.0010
	Ring	0.0031	0.0091	0.0003	Ring	0.0031	0.0113	0.0005	Ring	0.0031	0.0146	0.0009
MP2/cc-pVTZ	$C_2\cdots O_4$	0.0050	0.0206	0.0012	$O_6\cdots O_8$	0.0052	0.0222	0.0012	$C_2\cdot\cdot O_4$	0.0050	0.0208	0.0012
	$C_3\cdots S_5$	0.0045	0.0163	0.0009	$C_1\cdots O_6$	0.0052	0.0201	0.0012	$O_6\cdots O_8$	0.0052	0.0225	0.0013
	$C_2\cdots S_9$	0.0049	0.0172	0.0010	$C_1\cdots S_9$	0.0045	0.0161	0.0009	$O_4\cdots O_8$	0.0056	0.0243	0.0014
	Ring	0.0024	0.0085	0.0005	Ring	0.0025	0.0097	0.0006	Ring	0.0026	0.0116	0.0007

[a] The third bond critical point has not been localized at this level of theory.

Table S3 (cont.).

	MIV				MV				MVI			
	Critical Points	**(r_c)**	**$^2(r_c)$**	**$H(r_c)$**	**Critical Points**	**(r_c)**	**$^2(r_c)$**	**$H(r_c)$**	**Critical Points**	**(r_c)**	**$^2(r_c)$**	**$H(r_c)$**
MP2/6-31G(d,p)	$O_4\cdots O_8$	0.0061	0.0252	0.0010	$O_4\cdots S_7$	0.0063	0.0251	0.0010	$S_7\cdots S_9$	0.0039	0.0137	0.0009
	$C_2\cdots O_8$	0.0062	0.0251	0.0010	$C_1\cdots S_9$	0.0038	0.0118	0.0007	$S_5\cdots S_7$	0.0039	0.0137	0.0009
	$O_4\cdots O_6$	0.0063	0.0260	0.0010	$C_2\cdots O_8$	0.0058	0.0229	0.0010	$S_5\cdots S_9$	0.0039	0.0137	0.0009
	Ring	0.0028	0.0143	0.0008	Ring	0.0014	0.0056	0.0004	Ring	0.0019	0.0060	0.0004
MP2/cc-pVDZ	$O_4\cdots O_8$	0.0056	0.0234	0.0011	$O_4\cdots S_7$	0.0065	0.0242	0.0010	$S_7\cdots S_9$	0.0048	0.0134	0.0006
	$C_2\cdots O_8$	0.0058	0.0223	0.0010	$S_5\cdots S_9$	0.0046	0.0119	0.0005	$S_5\cdots S_7$	0.0048	0.0134	0.0006
	$O_4\cdots O_6$	0.0057	0.0237	0.0011	$C_2\cdots O_8$	0.0055	0.0205	0.0009	$S_5\cdots S_9$	0.0048	0.0134	0.0006
	Ring	0.0026	0.0125	0.0008	Ring	0.0015	0.0063	0.0004	Ring	0.0024	0.0070	0.0004
MP2/aug-cc-pVDZ	$C_1\cdots O_8$	0.0063	0.0240	0.0010	$O_4\cdots S_7$	0.0074	0.0281	0.0011	$S_7\cdots S_9$	0.0062	0.0182	0.0008
	$C_2\cdots O_8$	0.0067	0.0226	0.0008	$C_1\cdots S_9$	0.0060	0.0163	0.0006	$S_5\cdots S_7$	0.0062	0.0182	0.0008
	$C_2\cdots O_4$	0.0062	0.0237	0.0010	$C_2\cdots O_8$	0.0063	0.0203	0.0007	$S_5\cdots S_9$	0.0062	0.0182	0.0008
	Ring	0.0032	0.0132	0.0007	Ring	0.0024	0.0082	0.0004	Ring	0.0033	0.0096	0.0004
MP2/cc-pVTZ	$C_1\cdots O_8$	0.0050	0.0208	0.0011	$O_4\cdots S_7$	0.0060	0.0260	0.0015	$S_7\cdots S_9$	0.0049	0.0173	0.0011
	$C_2\cdots O_8$	0.0052	0.0206	0.0012	$C_1\cdots S_9$	0.0047	0.0165	0.0011	$S_5\cdots S_7$	0.0049	0.0173	0.0011
	$C_2\cdots O_4$	0.0050	0.0211	0.0012	$S_7\cdots O_8$	0.0051	0.0190	0.0011	$S_5\cdots S_9$	0.0049	0.0173	0.0011
	Ring	0.0025	0.0100	0.0006	Ring	0.0018	0.0061	0.0004	Ring	0.0024	0.0079	0.0005

Table S4. Dissociation energies[a] (kcal·mol^{-1}/cm^{-1}) calculated with the 6-31G(d,p) and the cc-pVDZ basis sets at different theoretical levels for the minima structures located on the potential energy surface of $(OCS)_3$.

		Method		
Structure	**Basis set**	**MP2**	**MP4SDTQ[b]**	**QCISD(T)[b]**
MI				
	6-31G(d,p)	3.7 / 1296	3.7 / 1310	2.5 / 894
	cc-pVDZ	3.8 / 1342	3.6 / 1289	2.5 / 892
MII				
	6-31G(d,p)	3.8 / 1344	3.9 / 1372	3.1 / 1075
	cc-pVDZ	3.6 / 1259	3.5 / 1229	2.7 / 950
MIII				
	6-31G(d,p)	4.1 / 1437	4.3 / 1478	3.6 / 1259
	cc-pVDZ	3.5 / 1225	3.5 / 1232	2.9 / 1038
MIV				
	6-31G(d,p)	3.9 / 1362	4.0 / 1394	3.0 / 1038
	cc-pVDZ	3.8 / 1353	3.8 / 1328	2.8 / 971
MV				
	6-31G(d,p)	3.1 / 1070	3.2 / 1099	2.5 / 862
	cc-pVDZ	3.2 / 1114	3.1 / 1089	2.4 / 854
MVI				
	6-31G(d,p)	1.6 / 558	1.5 / 529	1.2 / 408
	cc-pVDZ	2.0 / 709	1.8 / 624	1.4 / 479

[a] Zero-point energy correction estimated at the MP2/6-31G(d,p) and MP2/cc-pVDZ level, respectively.
[b] MP4SDTQ//MP2 and QCISD(T)//MP2 single-point calculations.

Tabla S5. Contributions to the interaction energy of the isolated dimers and dimer faces in the MII trimer as computed by SAPT/aug-cc-pVDZ. All numbers in cm^{-1}. NCP and CPR mean uncorrected and CP-corrected (including fragment relaxation energies) interaction energies, respectively.

	Isolated Dimers			**MII**		
	OCS·OCS(a)[a]	**OCS·OCS(b)[b]**	**OCS·OCS(c)[b]**	**OCS·OCS(A)**	**OCS·OCS(B)**	**OCS·OCS(C)**
$E_{pol}^{(10)}$	-742	-446	-584	-409	-594	-606
$E_{pol,r}^{(12)}$	34	96	37	65	-33	40
$\mathbf{E_{pol}^{(1)}}$	**-708**	**-350**	**-547**	**-344**	**-627**	**-566**
$E_{ind,r}^{(20)}$	-835	-282	-601	-311	-769	-637
${}^{t}E_{ind}^{(22)}$	24	-24	0	-24	20	1
$\mathbf{E_{ind}^{(2)}}$	**-811**	**-306**	**-601**	**-335**	**-749**	**-636**
$E_{disp}^{(20)}$	-1420	-1007	-1257	-1064	-1380	-1267
$\mathbf{E_{disp}^{(2)}}$	**-1420**	**-1007**	**-1257**	**-1064**	**-1380**	**-1267**
$E_{exch}^{(10)}$	1413	806	1168	875	1346	1212
$E_{exch}^{(11)} + E_{exch}^{(12)}$	35	113	71	115	35	66
$\mathbf{E_{exch}^{(1)}}$	**1448**	**919**	**1239**	**990**	**1381**	**1278**
$E_{exch-ind,r}^{(20)}$	775	225	538	251	714	576
${}^{t}E_{exch-ind}^{(22)}$	-22	19	0	20	-19	0
$E_{exch-disp}^{(20)}$	162	78	125	86	155	130
$\mathbf{E_{exch}^{(2)}}$	**915**	**322**	**663**	**357**	**850**	**706**
$\delta E_{\text{int}}^{HF}$	-67	-49	-59	-61	-61	-60
E_{int}^{HF}	543	254	462	345	636	485
E_{int}^{CORR}	-1188	-725	-1024	-804	-1221	-1031
$\mathbf{E_{int}(SAPT)}$	**-645**	**-472**	**-561**	**-458**	**-585**	**-546**
E_{RELAX} [c]	0	2	1	3	2	3
$\mathbf{E_{int}^{SUP}(NCP)}$ [d]	**-888**	**-700**	**-789**	**-692**	**-817**	**-770**
$\mathbf{E_{int}^{SUP}(CPR)}$ [d]	**-559**	**-421**	**-490**	**-401**	**-505**	**-473**

[a] Experimentally reported structure (see structure (a) in Table 5 and Ref. 25).
[b] Unobserved structures located by *ab initio* exploration of the potential energy surface (see structures (b) and (c) in Table 5).
[c] Relaxation energy.
[d] MP2/aug-cc-pVDZ interaction energies.

Table S5 (cont.). Contributions to the interaction energy of the isolated dimers and dimer faces in the MIII trimer as computed by SAPT/aug-cc-pVDZ. All numbers in cm^{-1}. NCP and CPR mean uncorrected and CP-corrected (including fragment relaxation energies) interaction energies, respectively.

	Isolated Dimers		**MIII**		
	OCS·OCS(b)[a]	**OCS·OCS(c)**[a]	**OCS·OCS(A)**	**OCS·OCS(B)**	**OCS·OCS(C)**
$E_{pol}^{(10)}$	-446	-584	-422	-396	-514
$E_{pol,r}^{(12)}$	96	37	71	52	-4
$\mathbf{E_{pol}^{(1)}}$	**-350**	**-547**	**-351**	**-344**	**-518**
$E_{ind,r}^{(20)}$	-282	-601	-304	-286	-584
${}^{t}E_{ind}^{(22)}$	-24	0	-26	-29	-4
$\mathbf{E_{ind}^{(2)}}$	**-306**	**-601**	**-330**	**-315**	**-588**
$E_{disp}^{(20)}$	-1007	-1257	-1054	-1040	-1274
$\mathbf{E_{disp}^{(2)}}$	**-1007**	**-1257**	**-1054**	**-1040**	**-1274**
$E_{exch}^{(10)}$	806	1168	866	846	1180
$E_{exch}^{(11)} + E_{exch}^{(12)}$	113	71	116	112	74
$\mathbf{E_{exch}^{(1)}}$	**919**	**1239**	**982**	**958**	**1254**
$E_{exch-ind,r}^{(20)}$	225	538	245	233	523
${}^{t}E_{exch-ind}^{(22)}$	19	0	21	23	3
$E_{exch-disp}^{(20)}$	78	125	84	82	126
$\mathbf{E_{exch}^{(2)}}$	**322**	**663**	**350**	**338**	**652**
$\delta E_{\mathrm{int}}^{HF}$	-49	-59	-57	-47	-58
E_{int}^{HF}	254	462	329	350	546
E_{int}^{CORR}	-725	-1024	-788	-800	-1079
$\mathbf{E_{int}(SAPT)}$	**-472**	**-561**	**-459**	**-450**	**-533**
E_{RELAX}[b]	2	1	3	5	2
$\mathbf{E_{int}^{SUP}(NCP)}$[c]	**-700**	**-789**	**-693**	**-687**	**-761**
$\mathbf{E_{int}^{SUP}(CPR)}$[c]	**-421**	**-490**	**-404**	**-399**	**-460**

[a] Unobserved structures located by *ab initio* exploration of the potential energy surface (see structures (b) and (c) in Table 5).
[b] Relaxation energy.
[c] MP2/aug-cc-pVDZ interaction energies.

Table S5 (cont.). Contributions to the interaction energy of the isolated dimers and dimer faces in the MV trimer as computed by SAPT/aug-cc-pVDZ. All numbers in cm^{-1}. NCP and CPR mean uncorrected and CP-corrected (including fragment relaxation energies) interaction energies, respectively.

	Isolated Dimer	**MV**
	OCS·OCS(c)[a]	**OCS·OCS**
$E_{pol}^{(10)}$	-584	-636
$E_{pol,r}^{(12)}$	37	44
$\mathbf{E_{pol}^{(1)}}$	**-547**	**-592**
$E_{ind,r}^{(20)}$	-601	-685
${}^{t}E_{ind}^{(22)}$	0	4
$\mathbf{E_{ind}^{(2)}}$	**-601**	**-681**
$E_{disp}^{(20)}$	-1257	-1300
$\mathbf{E_{disp}^{(2)}}$	**-1257**	**-1300**
$E_{exch}^{(10)}$	1168	1265
$E_{exch}^{(11)} + E_{exch}^{(12)}$	71	60
$\mathbf{E_{exch}^{(1)}}$	**1239**	**1325**
$E_{exch-ind,r}^{(20)}$	538	620
${}^{t}E_{exch-ind}^{(22)}$	0	-4
$E_{exch-disp}^{(20)}$	125	136
$\mathbf{E_{exch}^{(2)}}$	**663**	**752**
$\delta E_{\mathrm{int}}^{HF}$	-59	-65
E_{int}^{HF}	462	-499
E_{int}^{CORR}	-1024	-1059
$\mathbf{E_{int}(SAPT)}$	**-561**	**-560**
E_{RELAX} [b]	1	1
$\mathbf{E_{int}^{SUP}(NCP)}$ [c]	**-789**	**-782**
$\mathbf{E_{int}^{SUP}(CPR)}$ [c]	**-490**	**-481**

[a] Unobserved structures located by *ab initio* exploration of the potential energy surface (see structure (c) in Table 5).
[b] Relaxation energy.
[c] MP2/aug-cc-pVDZ interaction energies.