Supporting information to

The maximum occupancy condition for the localized property-optimized orbitals

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Appendix A. Identifiers of the molecules in the dataset[1] for which the total Lewis, as well as the total non-Lewis, orbital occupancies obtained by CLPO and NBO methods differs by more than 0.01e

Molecule identifier in the dataset	NBO6 total Lewis occupancy n_L^{NBO}	NBO6 total non-Lewis occupancy n_{nL}^{NBO}	CLPO total Lewis occupancy n_L^{CLPO}	CLPO total non-Lewis occupancy n_{nL}^{CLPO}	Note
0335	39.99154	2.00846	40.76688	1.23312	*a*
0240	40.04479	1.95521	40.71349	1.28651	*a*
0338	40.00236	1.99764	40.66306	1.33694	*a*
0340	40.04749	1.95251	40.66131	1.33869	*a*
1693	48.00041	1.99959	48.60204	1.39796	*a*
2851	47.97258	2.02742	48.50022	1.49978	*a*
6529	48.00152	1.99848	48.48117	1.51883	*a*
4661	50.46361	1.53639	50.74993	1.25007	*a*
7012	60.81514	1.18486	60.87651	1.12349	*b*
7071	60.82381	1.17619	60.87763	1.12237	*b*
7066	60.84115	1.15885	60.89469	1.10531	*b*
7069	60.93615	1.06385	60.98524	1.01476	*b*
6918	60.95097	1.04903	60.99839	1.00161	*b*
7070	62.99081	1.00919	63.01195	0.98805	*b*
5069	51.08712	0.91288	51.10008	0.89992	*b*
2320	53.27445	0.72555	53.28541	0.71459	*b*
2788	51.34036	0.65964	51.3511	0.6489	*b*
5827	53.29088	0.70912	53.30157	0.69843	*b*
2318	53.28864	0.71136	53.29931	0.70069	*b*
2560	51.35787	0.64213	51.36849	0.63151	*b*
6738	55.33038	0.66962	55.34093	0.65907	*b*
5071	55.20961	0.79039	55.22006	0.77994	*b*
0583	43.4223	0.5777	43.43268	0.56732	*b*
2324	55.34314	0.65686	55.35345	0.64655	*b*
5063	53.14388	0.85612	53.15401	0.84599	*b*
0496	45.39474	0.60526	45.40483	0.59517	*b*
5066	55.21747	0.78253	55.22753	0.77247	*b*
2782	53.32868	0.67132	53.33873	0.66127	*b*
7027	62.59087	1.40913	62.5807	1.4193	*c*

Notes:

[a] n_{nL}^{NBO} exceeds n_{nL}^{CLPO} by more than 0.1e (shown in Fig. 3 of the main text);

[b] n_{nL}^{NBO} exceeds n_{nL}^{CLPO} by more than 0.01e;

[c] n_{nL}^{CLPO} exceeds n_{nL}^{NBO} by more than 0.01e (shown in Fig. 3 of the main text).

[1] See https://github.com/andersx/ml-dftb3/tree/master/qm7 accessed Oct. 16, 2018

It is worth noting that for some of the molecules mentioned in the table, NBO log files report the presence of NBOs with unusually low occupancy, which nevertheless seem to be reported by the program as proper Lewis-type orbitals. The relevant lines of the dataset files are given below:

0240.log

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ------------------------------------------------------
...
   7. (0.99844) LP ( 1) C  2           s(  0.00%)p 1.00( 99.97%)d 0.00(  0.03%)
                                        0.0000  0.0000  0.0000 -0.0008  0.0000
                                        0.0009  0.0000  0.9998 -0.0101  0.0000
                                       -0.0074 -0.0148  0.0000  0.0000
```

0335.log

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ------------------------------------------------------
...
   7. (0.93799) LP ( 1) C  3           s(  0.00%)p 1.00( 99.95%)d 0.00(  0.05%)
                                        0.0000  0.0000  0.0008 -0.0597  0.0004
                                       -0.0363 -0.0002  0.9971 -0.0178  0.0003
                                        0.0163 -0.0158 -0.0016  0.0007
```

0338.log

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ------------------------------------------------------
...
   7. (0.94197) LP ( 1) C  1           s(  0.00%)p 1.00( 99.95%)d 0.00(  0.05%)
                                        0.0000  0.0000  0.0000 -0.0023  0.0000
                                        0.0009  0.0000  0.9996 -0.0186  0.0001
                                        0.0092 -0.0205  0.0000  0.0001
```

0340.log

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ------------------------------------------------------
...
   7. (1.00849) LP ( 1) C  1           s(  0.00%)p 1.00( 99.96%)d 0.00(  0.04%)
                                        0.0000  0.0001  0.0003  0.0128 -0.0001
                                       -0.0167  0.0001 -0.9995  0.0147 -0.0004
                                       -0.0110  0.0170 -0.0001 -0.0007
```

1693.log

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ------------------------------------------------------
...
   8. (1.01842) LP ( 1) C  5           s(  0.00%)p 1.00( 99.97%)d 0.00(  0.03%)
                                        0.0000  0.0002  0.0018 -0.0669  0.0003
                                        0.0023  0.0000 -0.9975  0.0136  0.0000
                                        0.0181  0.0000  0.0012 -0.0020
```

2851.log

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ------------------------------------------------------
...
   9. (1.06246) LP ( 1) C  5           s(  0.00%)p 1.00( 99.98%)d 0.00(  0.02%)
                                        0.0000  0.0003  0.0020 -0.0719  0.0005
                                        0.0030  0.0001 -0.9971  0.0163  0.0000
                                        0.0155  0.0002  0.0011 -0.0018
```

4661.log

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ------------------------------------------------------
...
  11. (1.11884) LP ( 1) C  7           s(  0.00%)p 1.00( 99.95%)d 0.00(  0.05%)
                                        0.0000  0.0069  0.0004  0.0115 -0.0002
                                        0.0433 -0.0006  0.9985 -0.0190  0.0006
                                        0.0080  0.0204 -0.0007 -0.0014
```

6529.log

```
     (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ------------------------------------------------------
...
  11. (1.19205) LP ( 2) N  5           s(  0.00%)p 1.00( 99.84%)d 0.00(  0.16%)
                                        0.0000  0.0002  0.0002 -0.0726  0.0005
                                       -0.0163  0.0005 -0.9964  0.0094  0.0006
                                        0.0393 -0.0001  0.0029 -0.0050
```

It is worth noting that in all these cases the highlighted orbital occupancy is not only 'quite low' from chemical-intuitive point of view, but is also below the occupancy threshold which is reported in the NBO log files and which is used to distinguish between the Lewis- and non-Lewis-type NBOs. Due to that it might be reasonable to consider the above mentioned NBOs as the non-Lewis-type ones which would further increase n_{nL}^{NBO}. For the sake of comparison we cite in the table below the occupancy thresholds reported in the NBO log files:

File name	Occupancy Threshold
0240.log	1.66
0335.log	1.65
0338.log	1.69
0340.log	1.69
1693.log	1.65
2851.log	1.72
4661.log	1.85
6529.log	1.69

Appendix B. NPA charges of the selected molecules shown in Figs. 3 and 4

The following tables contain the NPA charges extracted from the dataset files of the molecules containing sulfo group:

Fig. 3, *e* [**7027**]

Atom	NPA charge
C1	-0.68041
C2	-0.29539
C3	-0.36856
S4	**2.29002**
O5	-0.87738
O6	-0.89959
O7	-0.86991
H8	0.24918
H9	0.23878
H10	0.25821
H11	0.21906
H12	0.23743
H13	0.49854

Fig. 4, *a* [**7029**]

Atom	NPA charge
C1	-0.71789
C2	0.09404
C3	-0.39292
S4	**2.30232**
O5	-0.86204
O6	-0.86966
O7	-0.84367
H8	0.26451
H9	0.26302
H10	0.26189
H11	0.50040

Fig. 4, *b* [**7036**]

Atom	NPA charge
C1	-0.66576
C2	-0.09503
O3	-0.75871
S4	**2.29110**
C5	-0.88018
O6	-0.89411
O7	-0.89388
H8	0.23529
H9	0.22815
H10	0.22794
H11	0.21213
H12	0.21252
H13	0.25889
H14	0.25937
H15	0.26230

Fig. 4, *c* [**6948**]

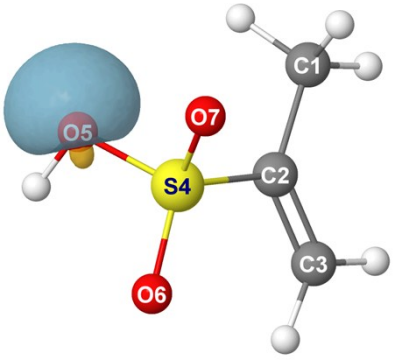
Atom	NPA charge
C1	-0.67618
C2	0.08529
C3	-0.68531
S4	**2.25541**
O5	-0.85476
O6	-0.85453
O7	-0.73573
H8	0.23658
H9	0.23423
H10	0.24415
H11	0.22708
H12	0.25918
H13	0.26459

Fig. 4, *d* [**7048**]

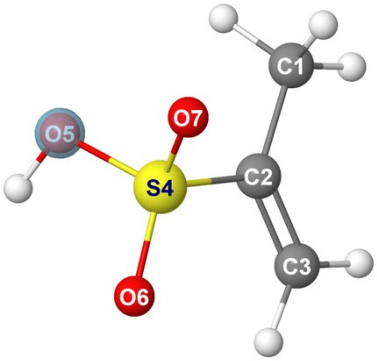
Atom	NPA charge
C1	-0.66641
C2	-0.66217
S3	**2.28544**
O4	-0.89582
O5	-0.89607
O6	-0.74272
C7	-0.28858
H8	0.23909
H9	0.23755
H10	0.23812
H11	0.26025
H12	0.26027
H13	0.21798
H14	0.20645
H15	0.20662

Appendix C. Selected localized orbitals (CLPOs) of the molecule with identifier 7027 (shown in Fig. 3, *e* in the main text)

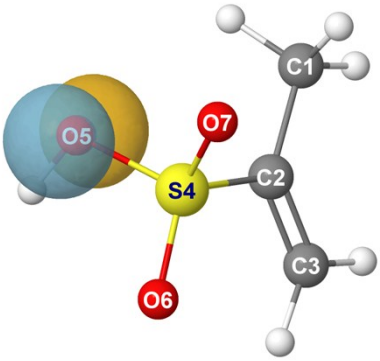
In the following figures we present the orbital isosurfaces correspond to 0.1 a.u. contour value corresponding to CLPOs related either to O atoms or their bonding to the S atom:



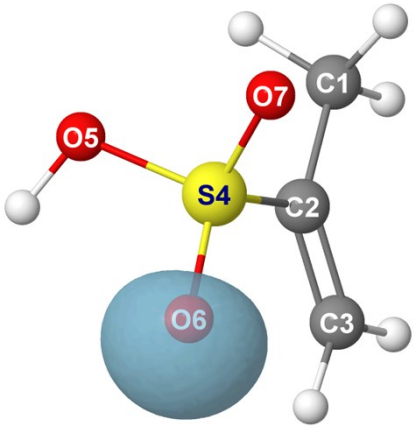
CLPO 70: (LP) O5, occ. 1.96854



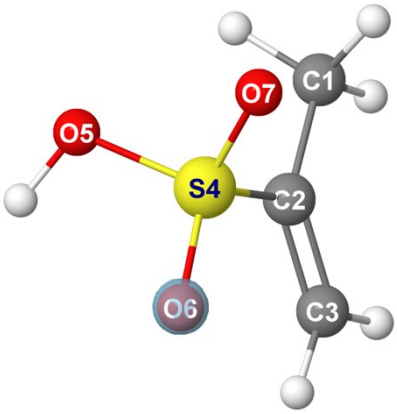
CLPO 71: (LP) O5, occ. 1.99978



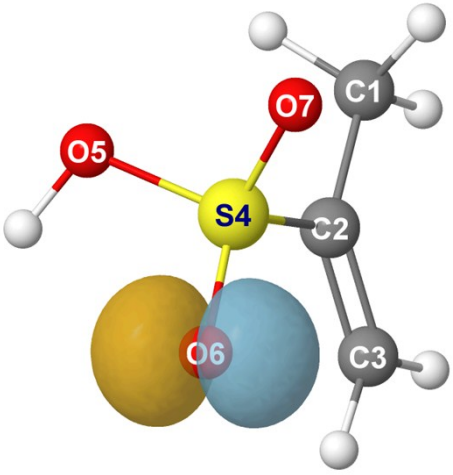
CLPO 77: (LP) O5, occ. 1.91296



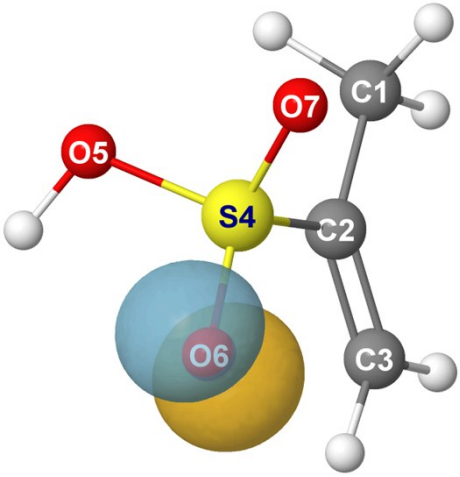
CLPO 84: (LP) O6, occ. 1.97641



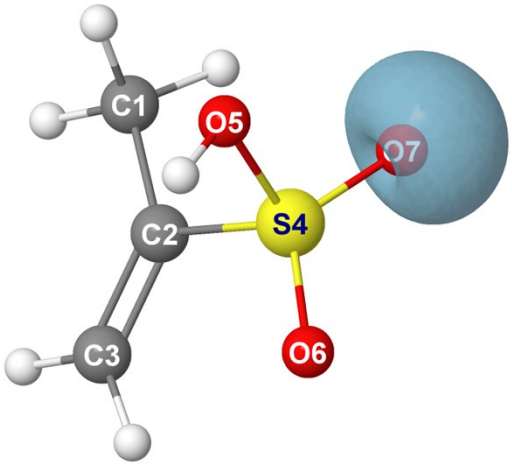
CLPO 85: (LP) O6, occ. 1.99986



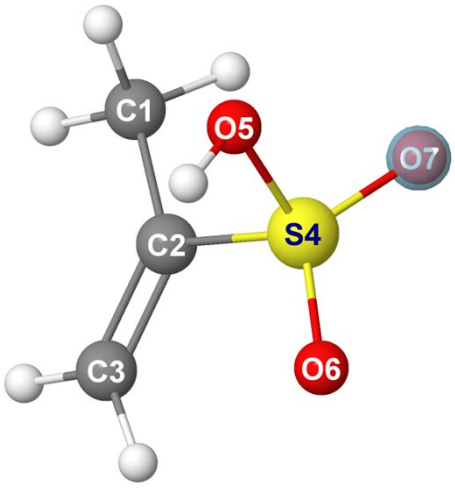
CLPO 89: (LP) O6, occ. 1.75801



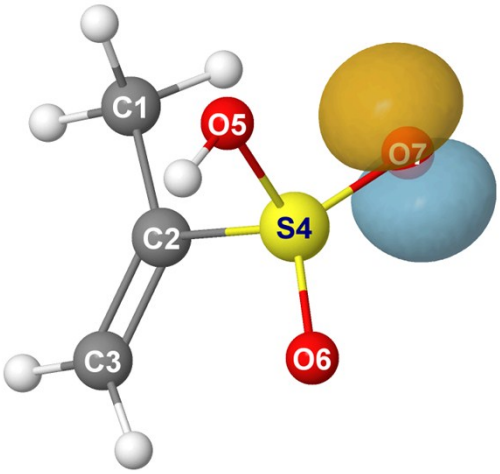
CLPO 90: (LP) O6, occ. 1.78154



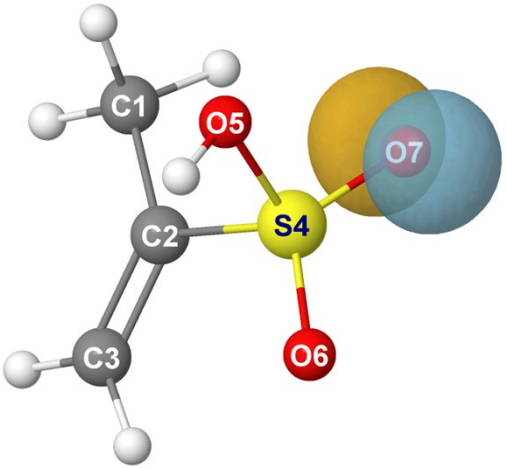
CLPO 97: (LP) O7, occ. 1.97696



CLPO 98: (LP) O7, occ. 1.99987

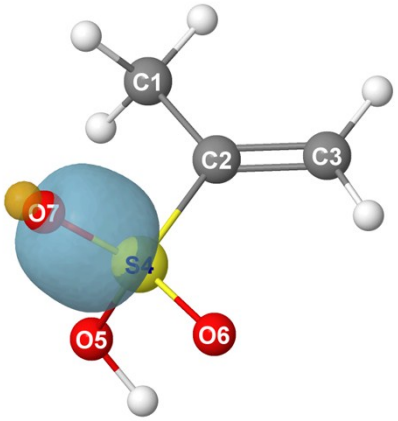


CLPO 102: (LP) O7, occ. 1.73676

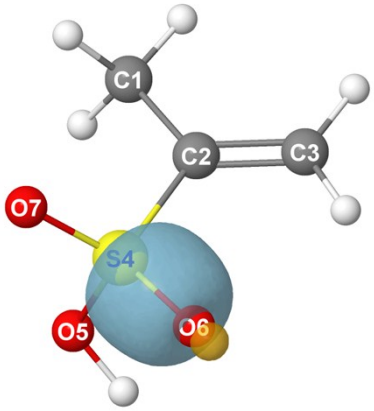


CLPO 103: (LP) O7, occ. 1.77664

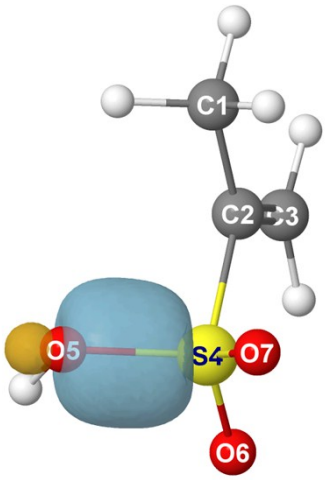
It follows from the performed CLPO analysis that each of O6 and O7 oxygen atoms has *three* lone pairs with occupancy of at least 1.73*e* (a core orbital with occupancy of almost 2.0*e*, also labeled as 'LP' in CLPO output, is not relevant for a discussion of bonding) This fact is consistent with the results of NPA population analysis indicating that each of these oxygen atoms has NPA charge of almost -0.9*e*, while the central S atom has NPA charge of about +2.3*e*. It can thus be concluded that S atom 'transfers' one of its electrons almost completely to each of the two O atoms, in this way establishing ionic (but not covalent) interaction in addition to the existing single covalent S–O bond. The latter bond is represented by CLPOs 50 and 57 shown below.



CLPO 50: (BD) S4-O7, occ. 1.98586



CLPO 57: (BD) S4-O6, occ. 1.98647



CLPO 59: (BD) S4-O5, occ. 1.98030