S1. Details on conformational sampling schemes.

Table S1 shows the steps that were used to generate the COSMO input files using the COSMOconf program. In the SMILES scheme, these correspond to default settings of COSMOconf. In the other schemes, various criteria have been significantly modified to allow a more thorough conformational sampling (at the expense of computing time). In the *SMILES* and *Best/Worst* schemes, the conformer set was generated using the BALLOON_CONF_GEN method of COSMOconf. The BALLOON_CONF_GEN conformer generation method uses a series of 7 Balloon steps to generate MMFF94 optimized structures. The CLUSTER_GEOCHECK method was then used to remove the duplicate conformers by comparing the geometries of the conformers. After BP/def-SV(P) level single-point calculations, the chemical potentials of the conformers in a pre-defined set of mixtures were compared using the CLUSTER_MU method, and conformers with similar chemical potentials were omitted. The COSMOconf program includes additional clustering methods to remove duplicates, but those were not tested here. In the *Systematic* scheme, the conformers were first generated using Spartan'14 and then input to the COSMOconf program. The conformer sampling implemented in Spartan'14 eliminates all of the duplicate conformers, which means that all of the conformers are initially unique. In this scheme, the first clustering steps and low level single-point calculations were skipped to make sure that no important conformers were eliminated. In all of the schemes, the geometries of the remaining conformers were further optimized at two different levels of theory; BP/def-SV(P) and BP/def-TZVP. (The def-SV(P) basis set has two basis functions per valence orbital and polarization functions on nonhydrogen atoms, while def-TZVP has three basis functions per valence orbital and polarization functions on all atoms – calculations with the latter are thus more accurate, but also more time-consuming.) The number of conformers was reduced after each optimization using the CLUSTER_GEOCHECK and CLUSTER_MU methods. To reduce the number of conformers even further, additional energy and number cut-offs (REDUCE_BY_E_MAX) were used before each geometry optimization and single-point calculation, using the cut-off values shown in Table S1. Generally, the cut-off energy was set high enough to make the number of conformers the tighter criterion. The final single-point energies were calculated using the same BP functional and a def2-TZVPD basis set (which contains three basis functions per valence orbital, and both polarization and diffuse functions on all atoms) with radii based isosurface cavity (FINE).

Table S1: The steps in the conformer sampling and COSMO calculations of three different calculation schemes using COSMOconf. All quantum chemical steps include COSMO solvation.

Method	*SMILES*	*Best/Worst*	*Systematic*
BALLOON_CONF_GEN	X	x	-
CLUSTER_GEOCHECK	X	x	-
REDUCE_BY_E_MAX	150 conformers or 2000 kcal/mol	-	-
BP-SV_P-COSMO-SP	x	x	-
CLUSTER_MU	x	x	-
REDUCE_BY_E_MAX	50 conformers or 25 kcal/mol	200 conformers or 40 kcal/mol	-
BP-SV_P-COSMO	x	x	x
CLUSTER_GEOCHECK and CLUSTER_MU	x	x	x
REDUCE_BY_E_MAX	12 conformers or 10 kcal/mol	120 conformers or 15 kcal/mol	150 conformers or 15 kcal/mol
BP-TZVP-COSMO	x	x	x
CLUSTER_GEOCHECK and CLUSTER_MU	x	x	x
REDUCE_BY_E_MAX	10 conformers or 6 kcal/mol	100 conformers or 10 kcal/mol	100 conformers or 10 kcal/mol
BP-TZVPD-FINE-COSMO-SP	x	x	x

S2. Vapor pressures for structural isomers 2-6 of $C_5H_{12}O_6$

Figure S1. Saturation vapor pressures, at 298.15 K, of different stereoisomers of structural isomer 2 of the dihydroxy dihydroperoxide $C_5H_{12}O_6$, at 298.15K, calculated using COSMOtherm version 18 and the BP_TZVPD_FINE_18 parametrization (based on BP/def2-TZVPD//BP/def-TZVP quantum chemical data), using different conformational sampling schemes.

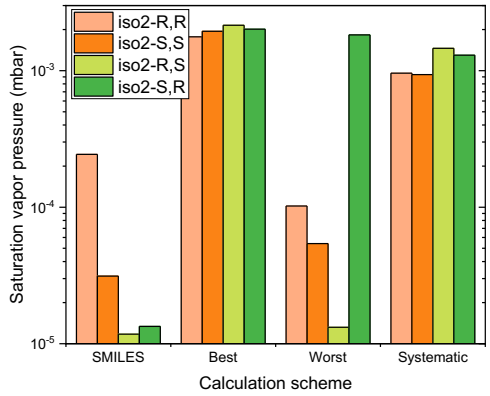


Figure S2. Saturation vapor pressures, at 298.15 K, of different stereoisomers of structural isomer 3 of the dihydroxy dihydroperoxide $C_5H_{12}O_6$, at 298.15K, calculated using COSMOtherm version 18 and the BP_TZVPD_FINE_18 parametrization (based on BP/def2-TZVPD//BP/def-TZVP quantum chemical data), using different conformational sampling schemes.

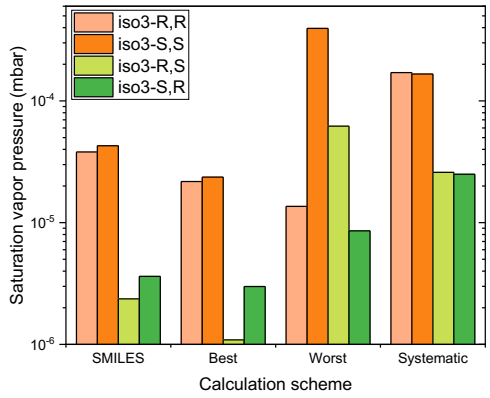
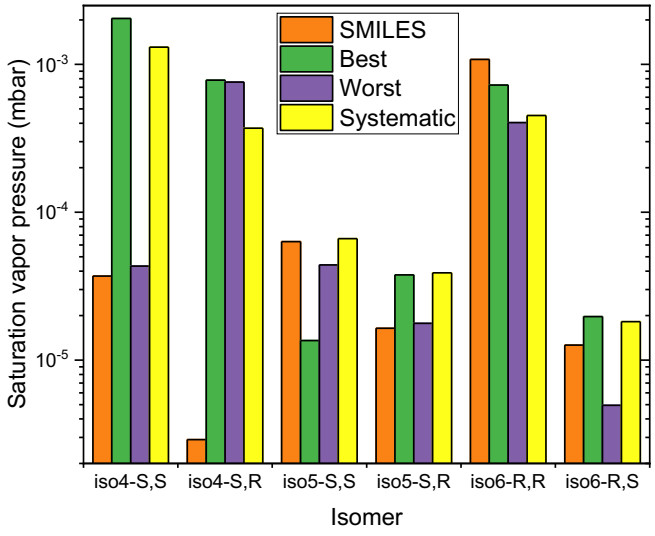


Figure S3. Saturation vapor pressures, at 298.15 K, of different stereoisomers of structural isomers 4-6 of the dihydroxy dihydroperoxide $C_5H_{12}O_6$, at 298.15K, calculated using COSMOtherm version 18 and the BP_TZVPD_FINE_18 parametrization (based on BP/def2-TZVPD//BP/def-TZVP quantum chemical data), using different conformational sampling schemes.



S3. Test results on scaling H-bonding parameters in COSMOTherm version 18

Figure S4: Logarithm of the saturation vapor pressure (in units of mbar) computed for the iso1-R,R isomer of $ISOP(OOH)_2$, using the ten best conformers identified by the *Systematic* sampling scheme, depending on the values of the three H-bonding parameters s0, c1 and c0. Calculated using COSMOtherm version 18 and the BP_TZVPD_FINE_18 parametrization (based on BP/def2-TZVPD//BP/def-TZVP quantum chemical data).

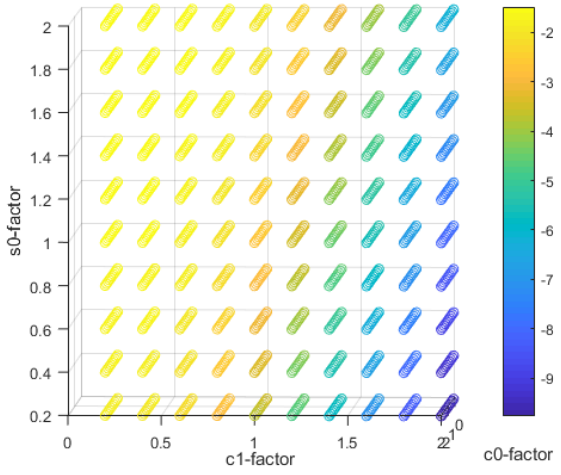
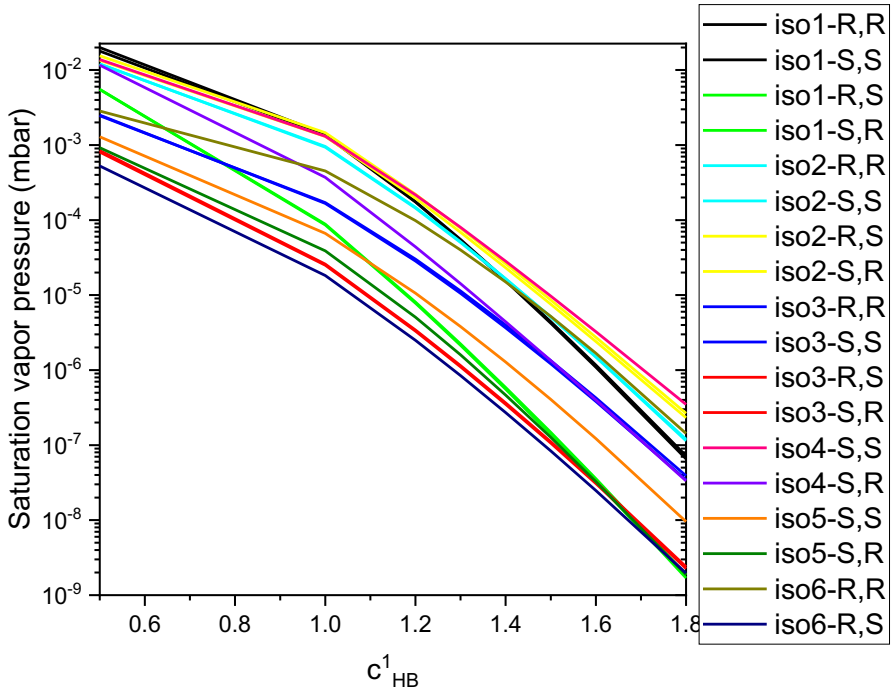


Figure S5. Dependence of the computed saturation vapor pressure, at 298.15 K, for all isomers of ISOP(OOH)$_2$, on the scaling factor c1. Calculated using COSMOtherm version 18 and the BP_TZVPD_FINE_18 parametrization (based on BP/def2-TZVPD//BP/def-TZVP quantum chemical data)



S4. Selection of conformers with a certain number of hydrogen bonds

The hydrogen bonding information was printed using the pr_steric option in the global command. The pr_steric option prints hydrogen bonding information of all atoms in the molecule that are available for forming intermolecular hydrogen bonds. All OH hydrogens (iele = 8) that have a positive partial charge (sighb < 0) are considered as hydrogen bond donors that are not fully hydrogen bonded in that conformer. In addition, the hydrogen bonded area (hbarea) was used to determine whether the hydrogen is partially hydrogen bonded (hbarea < 5.268) or not bonded (hbarea = 5.268; this is the threshold value for a completely unbonded hydrogen atom in COSMOTherm version 18). Based on this information, we counted the number of full and partial intramolecular hydrogen bonds. The partial intramolecular hydrogen bonds are simply all OH hydrogens with a hbarea < 5.268. Since all of our ISOP(OOH)$_2$ isomers have 4 hydrogen bond donors, the number of full intramolecular hydrogen bonds can be counted by subtracting the number of partially bonded and non-bonded hydrogens (sighb < 0) from four.