Extending the Applications of Circular Dichroism in Structure Elucidation: Tartrate Dianions Prefer Non-Symmetric Hydration / Hydrogen Bonding Aqueous Environment Breaks the Symmetry of a Tartrate Dianion

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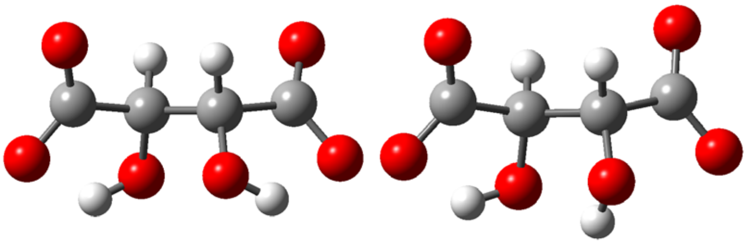
Supporting Information

DFT calculations

Isolated dianion of (R,R)-tartaric acid. Figure S1 presents structures of the dianion with C_2 and C_1 symmetry while Table S1 presents their relative energies. Independently on computational method Hartree-Fock (HF), Møller-Plesset second order perturbation theory (MP2), Becke's three parameter method with Lee-Young-Parr correlation-exchange potential (B3LYP), and on basis set used (6-31+G(d), 6-311++G(2df,2pd), aug-cc-pVTZ) the structure with C_2 symmetry is energetically favored by over 4 kcal mol^{-1}.



C_2 C_1

Figure S1. Structures of the isolated (*R*,*R*)-tartrate dianion possessing C_2 and C_1 symmetry

Table S1. Relative energies (kcal mol^{-1}) of the isolated dianion of (*R*,*R*)-tartaric acid with C_2 and C_1 symmetry. Various computational methods and basis sets used.

	C_2 symmetry	C_1 symmetry[a]
HF/6-31+g(d)[b]	0.00	4.20
MP2/6-31+g(d)[b]	0.00	4.01
B3LYP/6-31+g(d)[b]	0.00	4.43
HF/6-311++g(3df,2pd)[b]	0.00	4.58
B3LYP/6-311++g(3df,2pd)[b]	0.00	4.82
HF/aug-cc-pVTZ[b]	0.00	4.59
B3LYP/aug-cc-pVTZ[b]	0.00	4.81

[a] C_1 symmetric structure does not correspond to the potential energy minimum and converges to the C_2 symmetric structure. One HOCC torsion angle was frozen at the value obtained for the system with three water molecules.

[b] Absolute energies in Hartrees: HF/6-31+g(d) –602.979702; MP2/6-31+g(d) –604.619227; B3LYP/6-31+g(d) –606.246108; HF/6-311++g(3df,2pd) –603.186683; B3LYP/6-311++g(3df,2pd) –606.457085; HF/aug-cc-pVTZ –603.197705; B3LYP/aug-cc-pVTZ –606.468677.

Dianion of (R,R)-tartaric acid with one water molecule. Figure S2 presents structures of the dianion corresponding to the potential energy minima, while Table S2 presents their relative energies. In the lowest energy structure, conformation **C**, water molecule interacts with the dianion via two charge assisted hydrogen bonds formed at one terminal carboxylate moiety. In this structure (*R*,*R*)-tartrate dianion is almost of C_2 symmetry. However, among the structures where water molecule is involved not only in the interactions with the terminal COO$^-$ group but also in the interactions with the hydroxy groups, the structure **B** possessing C_1 symmetry is energetically favored by about 1 kcal mol^{-1} over the structure **A** with C_2 symmetry.

Table S2. Relative energies (kcal mol^{-1}) of the dianion of (*R*,*R*)-tartrate interacting with one water molecule. Various computational methods and basis sets used.

	A	**B**	**C** [a]	**D** [a]
	C_2	C_1		
HF/6-31+g(d)[b]	6.87	4.76	0.00	4.80
MP2/6-31+g(d)[b]	4.29	3.50	0.00	3.13
B3LYP/6-31+g(d)[b]	5.12	4.29	0.00	3.10
HF/6-311++g(3df,2pd)[b]	7.05	5.14	0.00	5.40
B3LYP/6-311++g(3df,2pd)[b]	5.43	4.78	0.00	3.99
HF/aug-cc-pVTZ[b]	7.09	5.21	0.00	5.33
B3LYP/aug-cc-pVTZ[b]	5.51	4.83	0.00	3.93

[a] dianion of (*R*,*R*)-tartaric acid in structures **C** and **D** is nearly of C_2 symmetry.

[b] Absolute energies in Hartrees: HF/6-31+g(d) –679.030463; MP2/6-31+g(d) –680.868127; B3LYP/6-31+g(d) –682.706294; HF/6-311++g(3df,2pd) –679.274215; B3LYP/6-311++g(3df,2pd)[b] –682.955311; HF/aug-cc-pVTZ –679.286919; B3LYP/aug-cc-pVTZ –682.968490

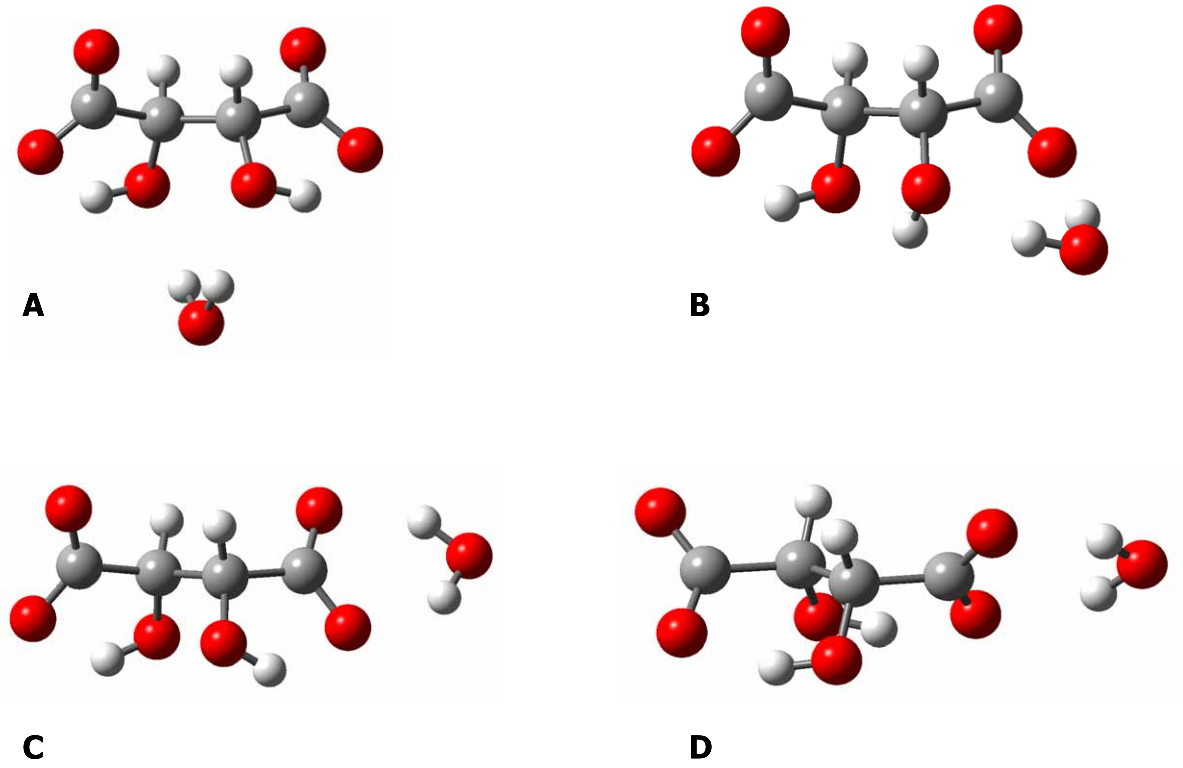


Figure S2. Structures of (*R*,*R*)-tartrate dianion interacting with one water molecule

Dianion of (R,R)-tartaric acid with two water molecules. Figure S3 presents structures of (*R*,*R*)-tartrate dianion interacting with two water molecules and Table S3 the corresponding relative energies. In the lowest energy structure **C** water molecules interact with carboxylate moieties, each at the opposite end of the dianion, via charge assisted hydrogen bonding. The structure **C** has C_2 symmetry, and OH groups attached to the central carbon atoms of tartrate dianion form intramolecular hydrogen bonds with their closest carboxylate oxygen atoms. The structures where water molecules interact with OH groups of tartrate dianion are higher in energy then structure **C**. The structure **B** is of C_1 symmetry and its relative energy is 3.6 kcal mol^{-1} at MP2/6-31+G(d), 4.5 kcal mol^{-1} at B3LYP/6-31+G(d), and 5.1 kcal mol^{-1} at B3LYP/aug-cc-pVTZ. The structure **A** is of C_2 symmetry is slightly higher in energy (about 1 kcal mol^{-1}) then the structure **B**.

Table S3. Relative energies (kcal mol^{-1}) of the dianion of (*R*,*R*)-tartrate interacting with two water molecules. Various computational methods and basis sets used.

	A	B	C	D
	C_2	C_1	C_2	C_1
HF/6-31+g(d)[a]	7.05	5.22	0.00	4.88
MP2/6-31+g(d)[a]	4.71	3.63	0.00	4.14
B3LYP/6-31+g(d)[a]	5.59	4.50	0.00	4.98
HF/6-311++g(3df,2pd)[a]	7.21	5.59	0.00	5.16
B3LYP/6-311++g(3df,2pd)[a]	5.87	5.00	0.00	5.36
HF/aug-cc-pVTZ[a]	7.25	5.67	0.00	5.25
B3LYP/aug-cc-pVTZ[a]	5.95	5.07	0.00	5.43

[a] Absolute energies in Hartrees: HF/6-31+g(d) –755.080309; MP2/6-31+g(d) –757.115829; B3LYP/6-31+g(d) –759.165141; HF/6-311++g(3df,2pd) –755.360903; B3LYP/6-311++g(3df,2pd) –759.452284; HF/aug-cc-pVTZ –755.375284; B3LYP/aug-cc-pVTZ –759.467045

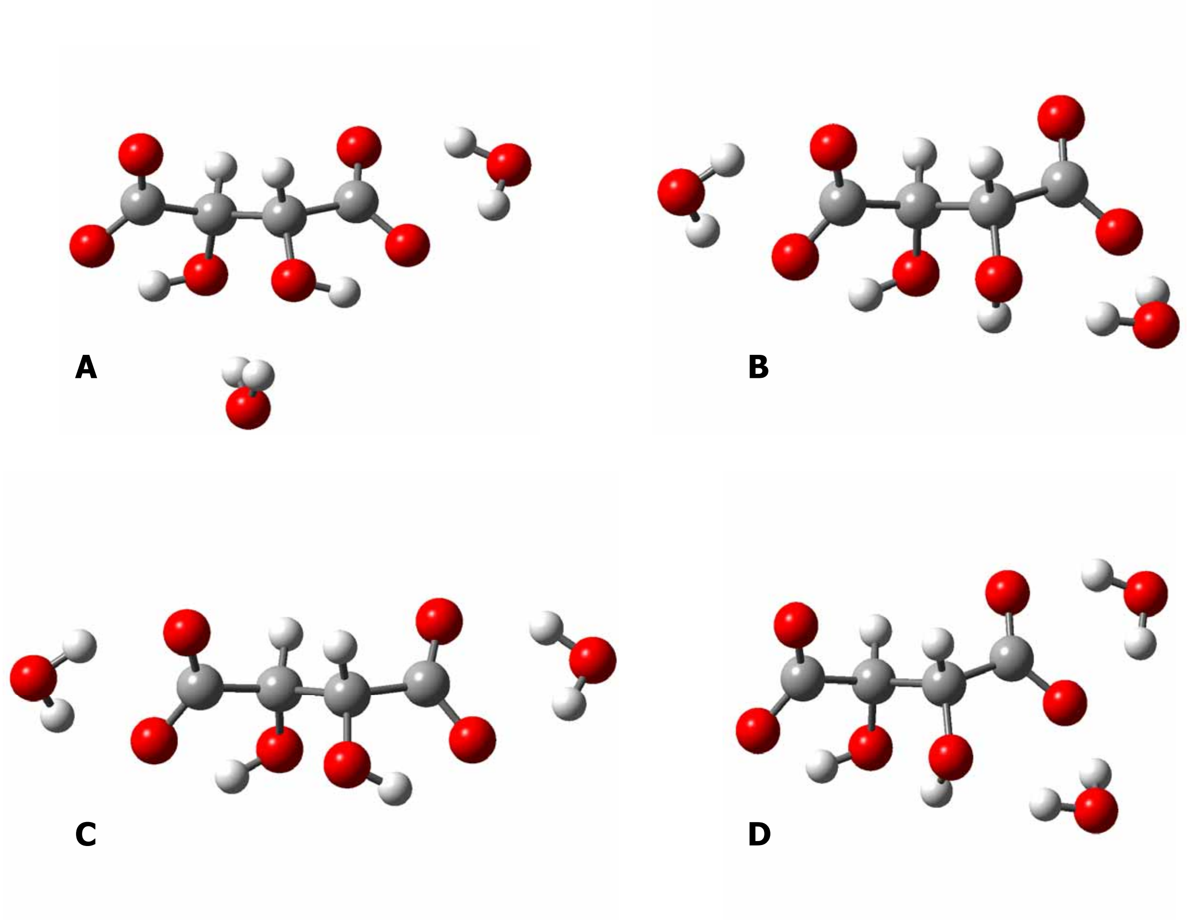


Figure S3. Structures of (*R*,*R*)-tartrate dianion interacting with two water molecules

Dianion of (R,R)-tartaric acid with three water molecules. In the case of (*R*,*R*)-tartrate dianion interacting with three water molecules the lowest energy structure is the structure **B** which has C_1 symmetry. The structure **A** which has C_2 symmetry is higher in energy by 0.8 kcal mol^{-1} as calculated at 6-31+G(d) basis set with MP2 and B3LYP methods, and 0.65 kcal mol^{-1} at much larger basis sets with B3LYP method. Calculations at HF level neglecting dynamic correlation of electrons overestimate relative energy of the structure **A**. It is worth to note that all low energy structures posses the common feature that is two water molecules form charge assisted hydrogen bonds at both ends of the dianion. The third water molecule interacts with one or two OH groups of tartrate dianion. Interestingly such interaction favors symmetry breaking in (*R*,*R*)-tartrate dianion.

Table S4. Relative energies (kcal mol^{-1}) of the dianion of (*R*,*R*)-tartrate interacting with three water molecules. Various computational methods and basis sets used.

	A	**B**	**C**	**D**	**E**
	C_2	C_1	C_2	C_1	C_1
HF/6-31+g(d)[a]	1.75	0.00	5.30	4.46	3.42
MP2/6-31+g(d)[a]	0.78	0.00	2.78	4.59	4.47
B3LYP/6-31+g(d)[a]	0.80	0.00	3.47	5.27	4.48
HF/6-311++g(3df,2pd)[a]	1.58	0.00	5.84	3.82	2.70
B3LYP/6-311++g(3df,2pd)[a]	0.65	0.00	4.29	4.76	3.89
HF/aug-cc-pVTZ[a]	1.53	0.00	5.84	3.75	2.55
B3LYP/aug-cc-pVTZ[a]	0.65	0.00	4.30	4.71	3.75

[a] Absolute energies in Hartrees: HF/6-31+g(d) –831.120601; MP2/6-31+g(d) –833.355544; B3LYP/6-31+g(d) –835.614389; HF/6-311++g(3df,2pd) –831.437597; B3LYP/6-311++g(3df,2pd) –835.939057; HF/aug-cc-pVTZ –831.453502; B3LYP/aug-cc-pVTZ –835.955271

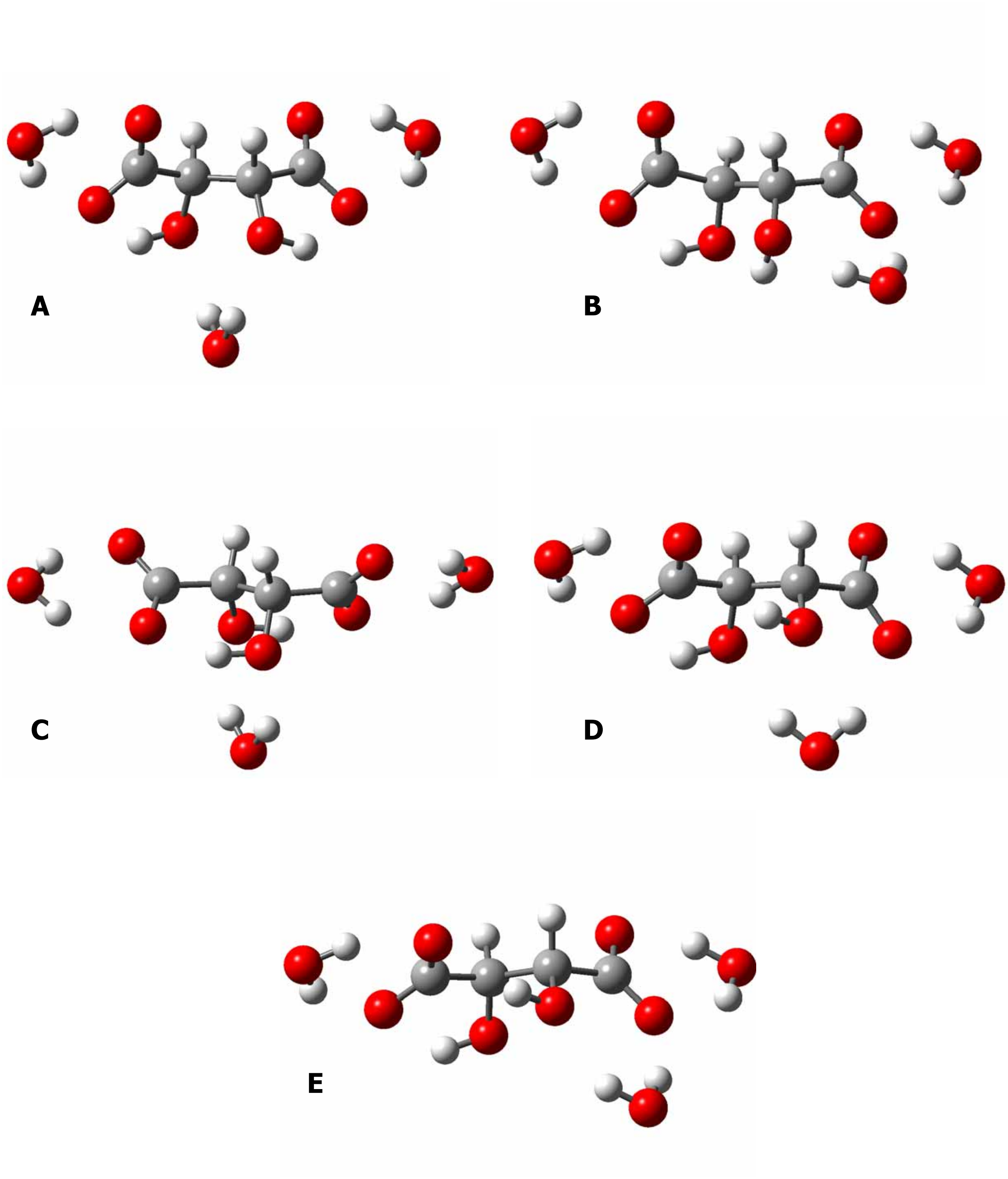


Figure S4. Structures of (*R*,*R*)-tartrate dianion interacting with three water molecules

Dianion of (R,R)-tartaric acid with many water molecules. Three layer ONIOM method was employed to obtain the result for (*R*,*R*)-tartrate dianion surrounded by fifty explicit water molecules treated quantum mechanically, and additional 108 water molecules treated at low level that provided mechanical embedding. Figure S5 presents (*R*,*R*)-tratrate dianion with C_2 and C_1 symmetry surrounded by water molecules. Energies obtained form ONIOM calculations for tartrate dianion (model system) at B3LYP/6-31+G(d) (high level) and tartrate dianion surrounded by 50 water molecules (middle system) at HF/STO-3G (medium level) are presented in Table S5. Although the isolated tartrate dianion favors C_2 symmetry by 3.9 kcal mol^{-1}, the tartrate dianion of C_1 symmetry surrounded by 50 water moleculs is energetically preferred by 9.2 kcal mol^{-1}. Moreover, when C_2 symmetry constraints imposed on (*R*,*R*) tartrate dianion were released, the subsequent optimization led to C_1 symmetry of the dianion.

Table S4. Relative energies (kcal mol^{-1}) dianion of (*R*,*R*)-tartrate interacting with many explicit water molecules. ONIOM components[a] for high level model system and medium level middle system shown.

	C_2	C_1
(*R*,*R*)-tartrate dianion	-3.87	0.00
dianion with 50 water molecules	9.19	0.00
Two layer ONIOM (QM:QM)	13.93	0.00
three layer ONIOM (QM:QM:MM)	18.80	0.00

[a] Absolute energies in Hartrees: method: low, system: model: 0.082963; method: med, system: model: -594.426960; method: low, system: mid: 807.943645; method: high, system: model: -606.177888; method: med, system: mid: -4344.179152; method: low, system: real: 818.043793; ONIOM (three layer): extrapolated energy -4345.829933

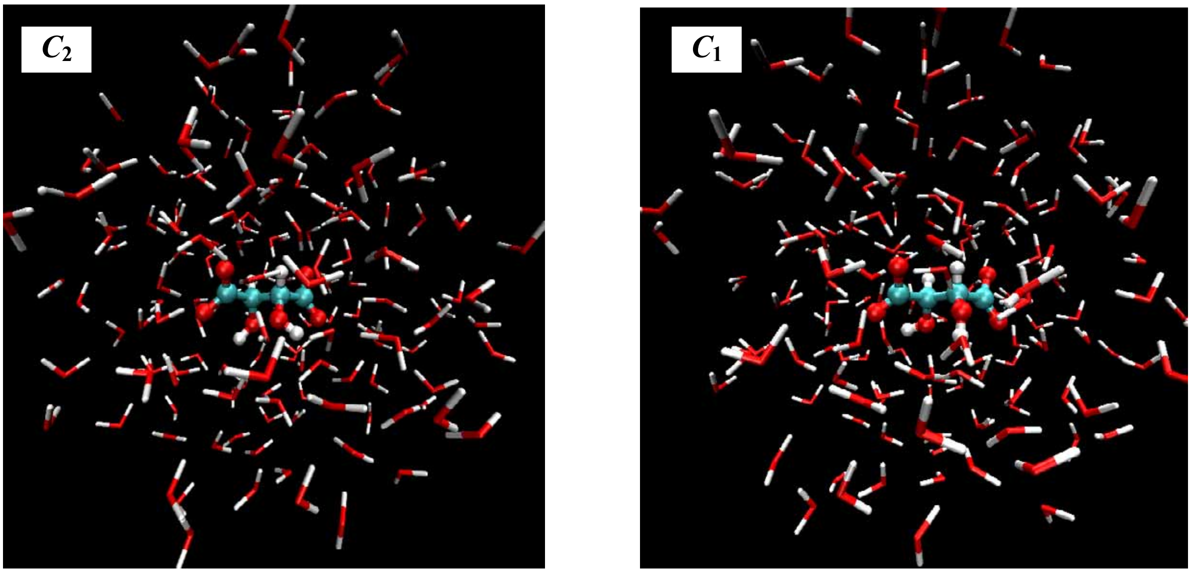


Figure S5. Structures of (*R*,*R*)-tartrate dianion interacting with many explicit water molecules (50 treated quantum mechanically and additional 108 constituting mechanical embedding treated at molecular mechanics level – UFF)

Aqueous solvent force divalent (*R*,*R*)-tartrate to break its C_2 symmetry which is energetically favored for the isolated molecule. In C_1 symmetry dianion one of the hydroxy groups is bound to form an intramolecular hydrogen bond with the proximal carboxylic oxygen atom while the other OH group is more free to rotate and more likely to be involved in intermolecular hydrogen bonds. Thus it appears that symmetry breaking due to the interactions with surrounding water molecules is a feature likely to be observed also for other dicarboxylic anions possessing multiple hydroxy groups in their structures.