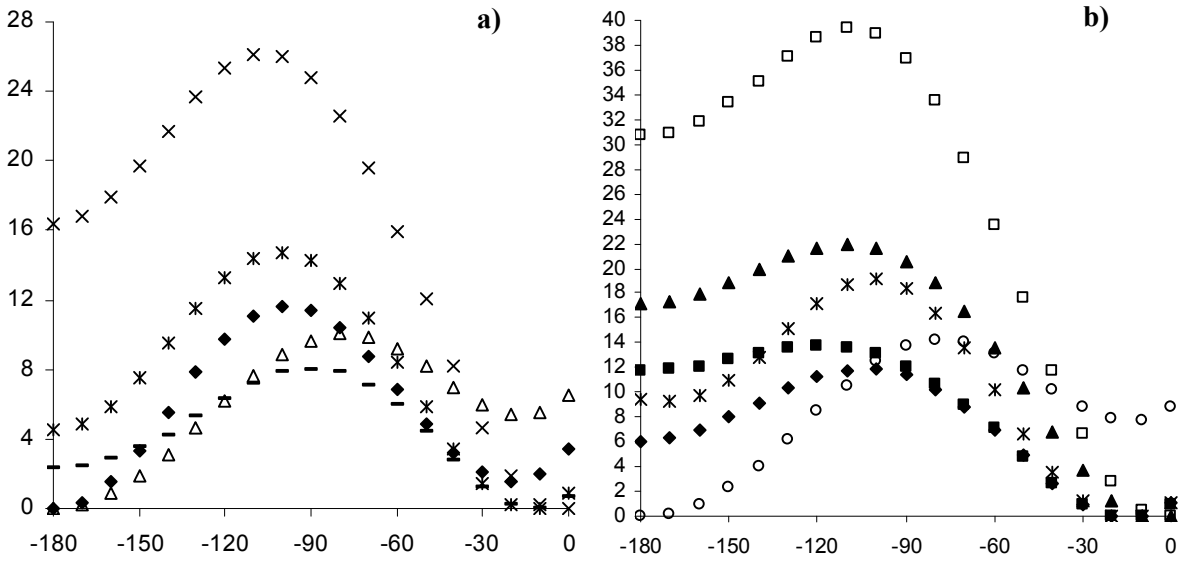

Figure S1: Energy profiles (in kJ mol^{-1}) for the internal rotation around C3-O3 bond (ω_1 in abscissas) (a) for the most stable rotamer of the different tautomers of neutral form: N5 (open triangles), N7 (-), N3´ (*), N4´ (boldface rhombs), and N5´ (x) (b) for the most stable rotamer of the different tautomers of anion form: A57 (open face circles), A54´ (boldface rhombs), A53´ (boldface triangles), A74´ (boldface squares), A3´4´ (*), A3´5´ (open face squares). These profiles are not shown for the tautomers A73´, A75´, A4´5´, and A55´.

TABLE S1: B3LYP/6-31++G(d,p) optimized O-H stretching vibrational frequencies (in cm^{-1}) and bondlengths (in Å) for all the hydroxyl groups of the most stable rotamer of delphinidin cation in the gas phase.

	3′-OH	4′-OH	5′-OH	3-OH	5-OH	7-OH
$\nu_{O\text{-}H}$	3757.8	3780.8	3835.1	3811.1	3812.4	3806.1
$r_{O\text{-}H}$	0.9702	0.9720	0.9665	0.9679	0.9681	0.9684

TABLE S2: Bondlengths for the most stable rotamers for the cation and for each tautomer of the neutral form of delphinidin.

		N4´	**N7**	**N5**	**N5´**	**N3´**	**N3**
	Casaaaa	*Nasaxas*	*Nasxsss*	*Naxsaaa*	*Nasaaax*	*Nasasxs*	*Nxsaaaa*
C5-C6	1.379	1.389	1.358	1.437	1.387	1.387	1.378
C6-C7	1.416	1.404	1.473	1.381	1.407	1.407	1.417
C5-C10	1.430	1.413	1.446	1.495	1.416	1.417	1.435
C9-C10	1.413	1.402	1.444	1.434	1.404	1.404	1.414
C4-C10	1.405	1.432	1.372	1.369	1.425	1.425	1.400
C8-C9	1.389	1.394	1.360	1.367	1.394	1.394	1.402
C7-C8	1.399	1.396	1.457	1.429	1.395	1.395	1.386
C3-C4	1.386	1.366	1.418	1.415	1.372	1.373	1.431
C2-C3	1.421	1.447	1.382	1.384	1.443	1.439	1.464
C2-C1'	1.442	1.400	1.463	1.463	1.417	1.418	1.446
C1'-C6'	1.422	1.445	1.410	1.414	1.431	1.440	1.416
C1'-C2'	1.418	1.446	1.415	1.411	1.443	1.426	1.417
C5'-C6'	1.384	1.364	1.392	1.389	1.403	1.380	1.387
C2'-C3'	1.385	1.363	1.387	1.390	1.376	1.402	1.386
C4'-C5'	1.405	1.451	1.398	1.397	1.451	1.401	1.397
C3'-C4'	1.409	1.455	1.398	1.400	1.407	1.458	1.404
C6-H6	1.085	1.085	1.087	1.086	1.085	1.085	1.086
C8-H8	1.084	1.085	1.083	1.082	1.085	1.085	1.085
H4-C4	1.087	1.086	1.087	1.090	1.086	1.086	1.084
C6'-H6'	1.080	1.078	1.079	1.081	1.077	1.077	1.085
C2'-H2'	1.081	1.081	1.083	1.081	1.080	1.081	1.082
C5-O5	1.352	1.366	1.370	1.245	1.364	1.365	1.361
C9-01	1.358	1.361	1.372	1.370	1.358	1.358	1.347
C7-O7	1.345	1.364	1.242	1.362	1.362	1.361	1.365
C2-01	1.351	1.379	1.369	1.365	1.371	1.369	1.352
C3-O3	1.360	1.365	1.373	1.375	1.360	1.364	1.259
C5'-O5'	1.367	1.359	1.364	1.378	1.281	1.370	1.378
C3'-O3'	1.353	1.356	1.377	1.363	1.368	1.278	1.366
C4'-O4'	1.347	1.255	1.368	1.367	1.326	1.327	1.367

TABLE S3: Bondlengths (in Å) for the most stable rotamer of the cation and for each tautomer of the anion of delphinidin

		A37	**A35**	**A55´**	**A33´**	**A34´**	**A35´**	**A4´5´**	**A57**	**A73´**	**A75´**	**A54´**	**A54´**	**A74´**
	Casaaaa	*Axsxaaa*	*Axxsaaa*	*Asxsaax*	*Axsasxs*	*Axaaxas*	*Axsaaax*	*Aasasxx*	*Aaxxsss*	*Assxsxs*	*Assxaax*	*Asxssxs*	*Aaxsxas*	*Aasxxas*
C5-C6	1.379	1.361	1.435	1.438	1.386	1.387	1.386	1.398	1.407	1.363	1.363	1.438	1.439	1.368
C6-C7	1.416	1.471	1.389	1.385	1.409	1.404	1.409	1.398	1.436	1.469	1.468	1.385	1.387	1.464
C5-C10	1.430	1.445	1.497	1.487	1.426	1.425	1.427	1.406	1.507	1.438	1.438	1.487	1.475	1.427
C9-C10	1.413	1.442	1.431	1.426	1.409	1.407	1.409	1.407	1.450	1.440	1.439	1.427	1.413	1.429
C4-C10	1.405	1.377	1.376	1.385	1.412	1.420	1.411	1.438	1.359	1.384	1.385	1.384	1.398	1.398
C8-C9	1.389	1.378	1.388	1.380	1.403	1.400	1.403	1.398	1.351	1.369	1.369	1.379	1.384	1.371
C7-C8	1.399	1.442	1.408	1.415	1.386	1.391	1.387	1.396	1.484	1.450	1.450	1.415	1.412	1.451
C3-C4	1.386	1.449	1.449	1.403	1.421	1.415	1.424	1.373	1.431	1.404	1.404	1.403	1.385	1.388
C2-C3	1.421	1.428	1.432	1.395	1.488	1.492	1.489	1.437	1.370	1.392	1.392	1.395	1.418	1.415
O1-C9	1.358	1.353	1.348	1.368	1.352	1.359	1.352	1.351	1.389	1.373	1.373	1.368	1.372	1.376
O1-C2	1.351	1.381	1.376	1.362	1.360	1.367	1.360	1.407	1.380	1.363	1.365	1.360	1.370	1.372
C2-C1'	1.442	1.448	1.449	1.453	1.429	1.411	1.431	1.409	1.465	1.455	1.453	1.455	1.425	1.426
C1'-C2'	1.418	1.418	1.418	1.410	1.431	1.441	1.434	1.449	1.414	1.411	1.410	1.411	1.434	1.434
C1'-C6'	1.422	1.418	1.417	1.423	1.429	1.438	1.429	1.436	1.412	1.423	1.423	1.422	1.434	1.434
C2'-C3'	1.385	1.389	1.389	1.399	1.403	1.367	1.383	1.384	1.388	1.420	1.399	1.420	1.372	1.373
C5'-C6'	1.384	1.387	1.387	1.420	1.388	1.371	1.411	1.417	1.392	1.401	1.420	1.401	1.374	1.374
C3'-C4'	1.409	1.399	1.399	1.385	1.447	1.444	1.395	1.478	1.394	1.441	1.385	1.441	1.438	1.438
C4'-C5'	1.405	1.394	1.394	1.442	1.391	1.437	1.437	1.466	1.397	1.384	1.442	1.384	1.434	1.434
C6-H6	1.085	1.089	1.088	1.088	1.087	1.084	1.087	1.086	1.086	1.088	1.088	1.088	1.088	1.088
C8-H8	1.084	1.084	1.082	1.082	1.086	1.086	1.086	1.086	1.085	1.084	1.084	1.082	1.082	1.084
C4-H4	1.087	1.086	1.087	1.086	1.084	1.088	1.084	1.085	1.090	1.085	1.085	1.086	1.090	1.088
C2'-H2'	1.081	1.082	1.082	1.083	1.082	1.083	1.081	1.080	1.084	1.084	1.083	1.084	1.082	1.082
C6'-H6'	1.080	1.087	1.087	1.087	1.081	1.082	1.081	1.078	1.080	1.085	1.087	1.085	1.079	1.079
C5-O5	1.352	1.379	1.253	1.253	1.374	1.374	1.374	1.379	1.267	1.378	1.378	1.253	1.259	1.384
C7-O7	1.345	1.257	1.380	1.375	1.381	1.383	1.381	1.378	1.260	1.252	1.252	1.375	1.379	1.256
C3-O3	1.360	1.277	1.274	1.367	1.260	1.261	1.257	1.368	1.382	1.372	1.370	1.369	1.382	1.384
C3'-O3'	1.353	1.377	1.377	1.381	1.292	1.369	1.383	1.295	1.385	1.283	1.380	1.283	1.369	1.369
C5'-O5'	1.367	1.390	1.389	1.283	1.383	1.372	1.293	1.268	1.373	1.382	1.284	1.381	1.372	1.372
C4'-O4'	1.347	1.386	1.386	1.363	1.351	1.274	1.353	1.305	1.381	1.364	1.364	1.364	1.278	1.278

TABLE S4: B3LYP/6-31++G(d,p) relative energies (in kJ mol^{-1}) in the gas phase and in aqueous solution for all the rotamers here studied for the anionic form of delphinidin.

	Rotamer	ΔE^{a}	ΔE^{b}	Rotamer	$\Delta E^{PCM\ a}$	E^{PCM}-$E^{gas\ b,c}$	$\Delta G_{sol.}{}^{c}$	$E_{pol.}{}^{c}$
A54´	*Asxsxas*	0.0	0.0	*Asxsxas*	9.6	-60.8	-61.3	-72.6
A74´	*Assxxas*	5.8	6.0	*Assxxas*	8.7	-62.3	-63.3	-74.7
A54´	*Aaxsxas*	6.2	4.0	*Aaxsxas*	0.0	-64.5	-63.1	-74.3
A54´	*Aaxaxas*	9.7	7.1	*Aaxaxas*	1.8	-64.9	-64.3	-75.5
A34´	*Axaaxas*	15.6	12.7	*Axaaxas*	11.0	-64.2	-65.5	-76.8
A74´	*Aasxxas*	17.7	15.1	*Aasxxas*	1.7	-66.9	-68.5	-79.6
A34´	*Axsaxas*	26.3	23.7	*Axsaxas*	1.7	-68.9	-72.5	-83.7
A34´	*Axssxas*	32.2	28.8	*Axssxas*	2.5	-70.1	-75.2	-86.4
A74´	*Aaaxxas*[d]	32.7	27.2	*Aaaxxas*	15.1	-67.3	-71.2	-82.4
A55´	*Asxsaax*	36.7	35.1	*Asxsaax*	31.5	-64.3	-65.8	-77.3
A53´	*Asxssxs*	40.2	38.7	*Aaxssxs*	29.5	-65.6	-71.3	-82.4
A55´	*Asxaaax*	40.6	38.6	*Asxaaax*	37.8	-63.7	-67.2	-78.6
A75´	*Assxaax*	41.9	40.4	*Aasxaax*	31.9	-65.4	-76.8	-87.8
A53´	*Asxasxs*	43.2	41.3	*Aaxasxs*	31.1	-65.9	-71.8	-82.9
A73´	*Assxsxs*	46.7	45.0	*Aasxsxs*	30.2	-67.0	-77.9	-89.0
A35	*Axxsaaa*	53.1	48.7	*Axxsaaa*	20.8	-70.8	-73.2	-84.4
A37	*Axsxaaa*	56.4	52.4	*Axsxaaa*	21.5	-71.4	-72.7	-83.8
A35	*Axxaaaa*	57.2	52.3	*Axxaaaa*	22.1	-71.4	-75.2	-86.4
A35	*Axxssss*	63.2	58.0	*Axxssss*	21.5	-73.0	-78.2	-89.4
A37	*Axsxsss*	64.1	59.6	*Axsxsss*	22.0	-73.1	-76.2	-87.3
A35	*Axxasss*	68.7	62.7	*Axxasss*	22.9	-74.0	-81.1	-92.3
A33´	*Axsasxs*	80.2	75.3	*Axsasxs*	33.0	-74.3	-80.8	-92.0
A33´	*Axsssxs*	87.5	81.6	*Axsssxs*	34.0	-75.8	-84.5	-95.7
A35´	*Axsaaax*	93.5	87.6	*Axsaaax*	36.8	-76.6	-86.6	-97.8
A57	*Aaxxsss*	97.7	92.1	*Aaxxsss*	28.0	-79.7	-86.0	-97.1

A35´	*Axssaax*	99.8	92.9	*Axssaax*	37.8	-77.9	-89.5	-100.6
A57	*Aaxxaaa*	101.3	95.2	*Aaxxaaa*	28.3	-80.5	-88.1	-99.2
A3´4´	*Aasaxxs*[d]	126.1	119.6	*Aasaxxs*	41.9	-83.2	-102.7	-113.8
A3´4´	*Aassxxs*[d]	134.0	126.6	*Aassxxs*	42.3	-85.0	-107.1	-118.2
A3´4´	*Aassxxs*[d]	134.0	126.6	*Aassxxs*	42.3	-85.0	-107.1	-118.2
A4´5´	*Aasaxax*[d]	137.0	130.4	*Aasaxax*	47.5	-84.4	-105.7	-116.9
A4´5´	*Aassxax*[d]	143.1	135.8	*Aassxax*	47.9	-85.8	-109.0	-120.1
A3´5´	*Aasasxx*	191.4	182.1	*Aasasxx*	77.5	-90.3	-116.9	-128.0
A3´5´	*Aasssxx*	198.9	188.4	*Aasssxx*	78.1	-91.9	-121.1	-132.1

[a] Energies are relative to the most stable conformer without they have not been corrected with ZPVE. This reference is: E(*Casaaaa*)= -1104.61397 au in gas phase and E (*Casaaaa*)= -1104.73253 au in the PCM modeled aqueous solvated.

[b] Energies are relative to the most stable conformer once they have been corrected with ZPVE. This reference is: E (+ZPVE)(*Casaaaa*)= -1104.37269 au.

[c] In kcal mol^{-1}.

[d] This rotamer presents one imaginary frequencies.