Conformational equilibria in *o*-anisic acid and its monohydrated complex, the prevalence of the *trans*-COOH form

Electronic Supplementary Information

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Table S33. r_s coordinates of the -COOD specie of C2 form compared to the B3LYP-D3/6-311++G(d,p) predicted r_e coordinates from the H_{15} atom of C1 and C2 conformers, which allows the confirmation of the C2 form identification.

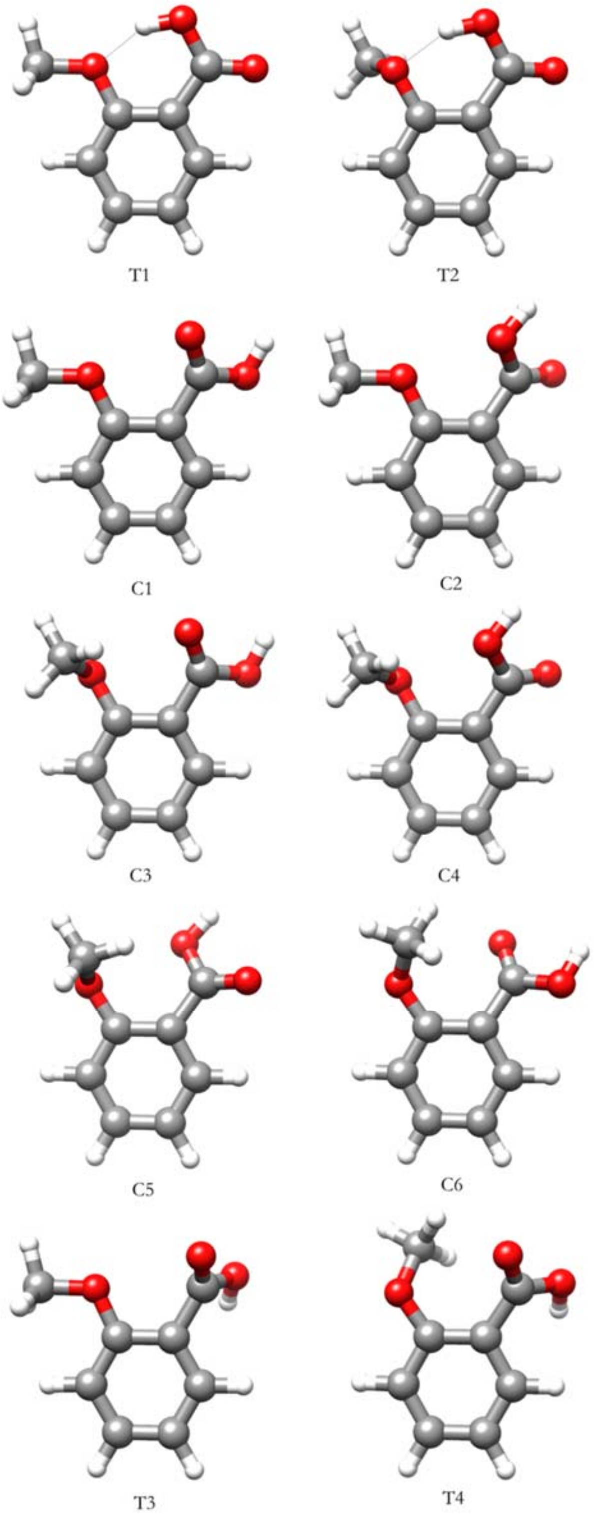
Table S34. Structure coordinates r_s, r_e, and $r_m^{(1L)}$ of the T1-w-1 *o*-anisic acid-water conformer.

Table S35. r_s, r_e, and $r_m^{(1L)}$ distances and angles determined for the T1 *o*-anisic acid conformer.

Table S36. r_s, r_e, and $r_m^{(1L)}$ distances and angles determined for the T1-w-1 *o*-anisic acid water complex.

Table S37. B3LYP-D3/6-311++G(d,p) predicted structural relaxation parameters (distances in Å and angles in degree) for some selected bond distances and angles along the coordinate τ.

Figure S1. Predicted conformers for *o*-anisic acid. The corresponding spectroscopy parameters are given in Table S1. The conformers were labelled as T*n* or C*n*, where T or C refer to the *trans* or *cis* arrangement of the –COOH group and *n* to the order of increasing MP2/6-311G++(d,p) energy.


T1 T2

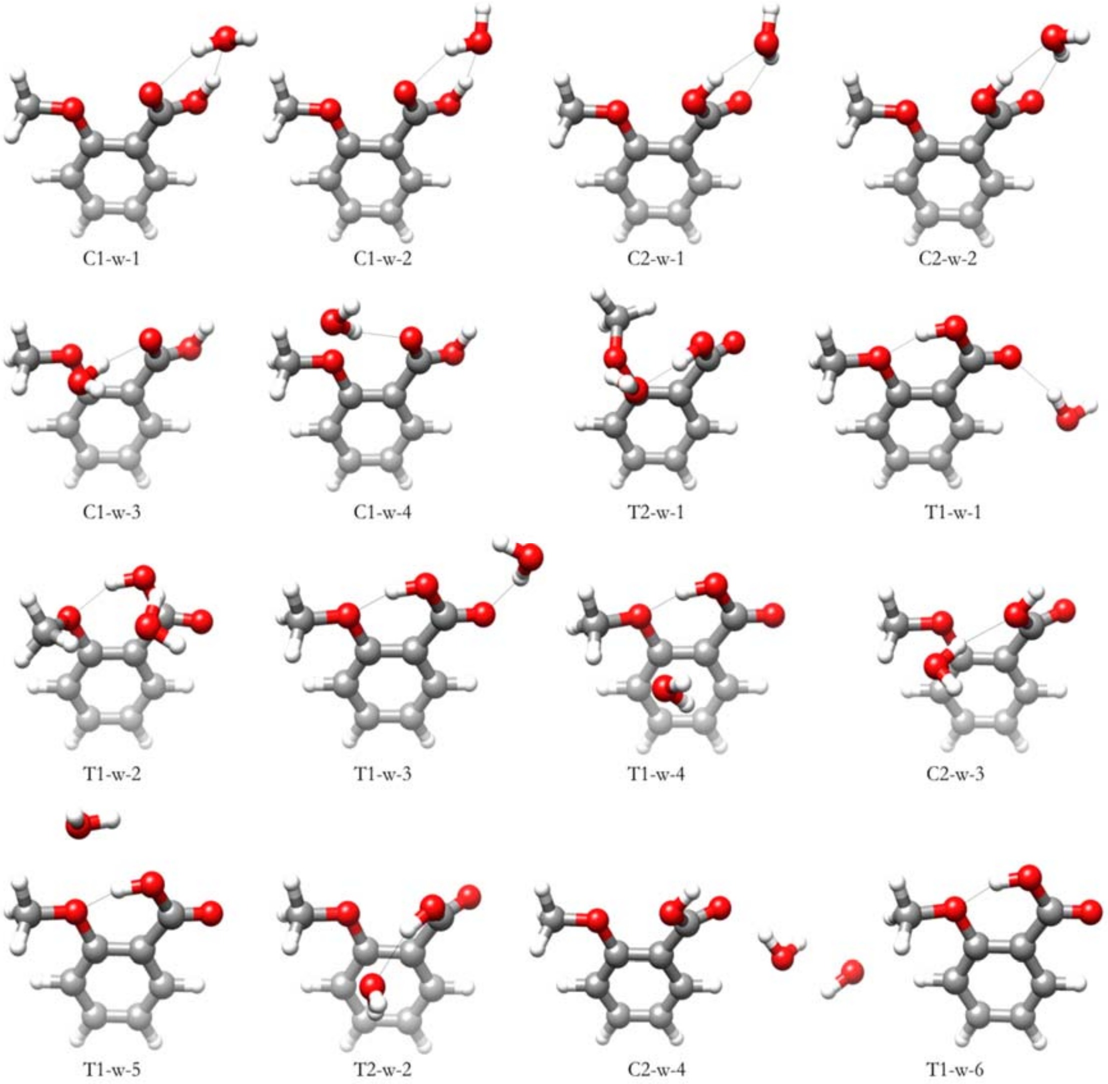
C1 C2

C3 C4

C5 C6

T3 T4

Figure S2. Predicted conformers for *o*-anisic acid-water complexes. The corresponding parameters are given in Table S2. The complexes were labeled as T*n*-w-*m* or C*n*-w-*m* where T*n* or C*n* refer to the monomer conformer and *m* to the order of increasing MP2/6-311++G(d,p) energy for each series of T*n*-w or C*n*-w complexes.



C1-w-1 C1-w-2 C2-w-1 C2-w-2

C1-w-3 C1-w-4 T2-w-1 T1-w-1

T1-w-2 T1-w-3 T1-w-4 C2-w-3

T1-w-5 T2-w-2 C2-w-4 T1-w-6

Figure S3. Predicted MP2/6-311++G(d,p) energy profile for the methoxy group torsion interconverting the T2 into the T1 conformer of *o*-anisic acid through a very small barrier. See Figure 3 for atom labeling.

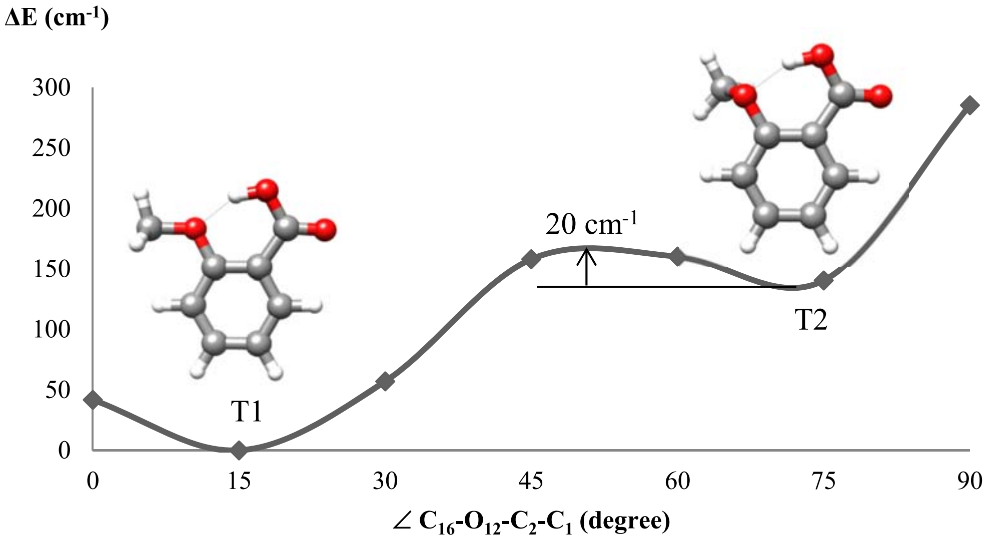
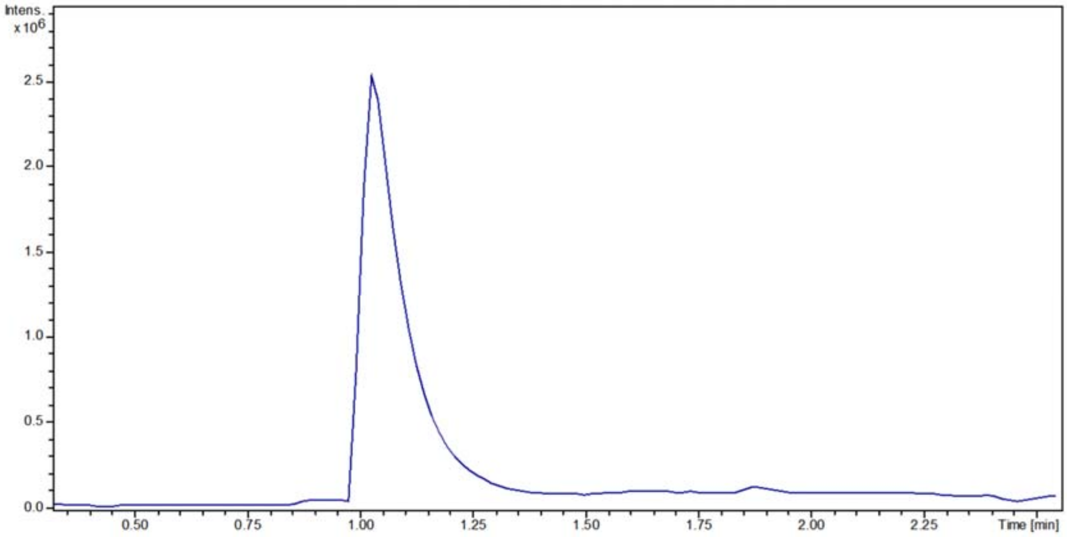
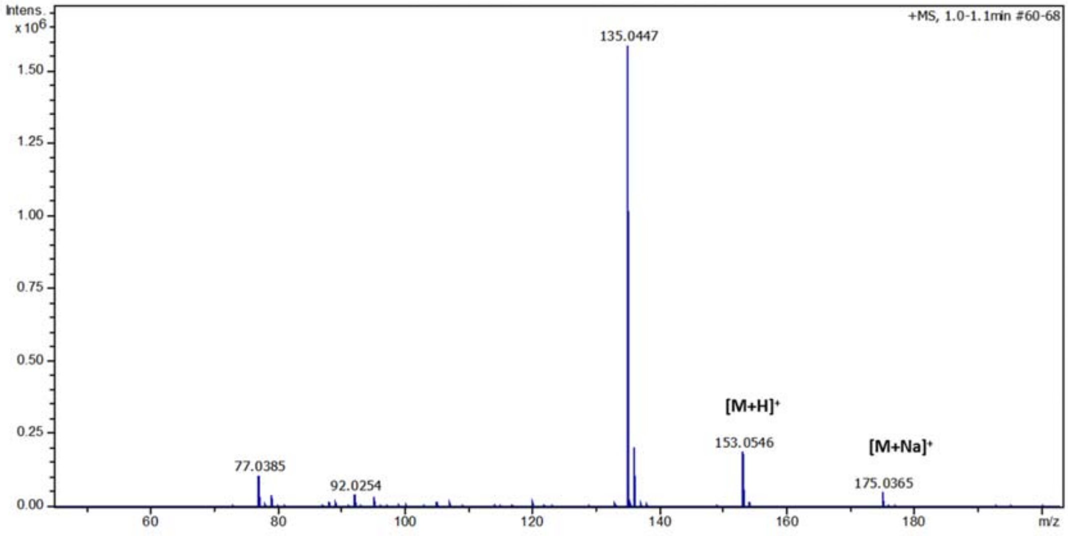


Figure S4. ESI-TOF results for the pure commercial sample of *ortho*-anisic acid.





Meas. m/z	m/z	err [ppm]	mSigma	Ion Formula
153,0546	153,0546	-0.0	7.4	C8H9O3
175,0365	175,0366	0.3	6.5	C8H8NaO3

Figure S5. GS-MS results for the sample residuals after heating and recording the rotational spectra. (a) solid residues in glass fiber. (b) Solid residues in the surface of the nozzle.

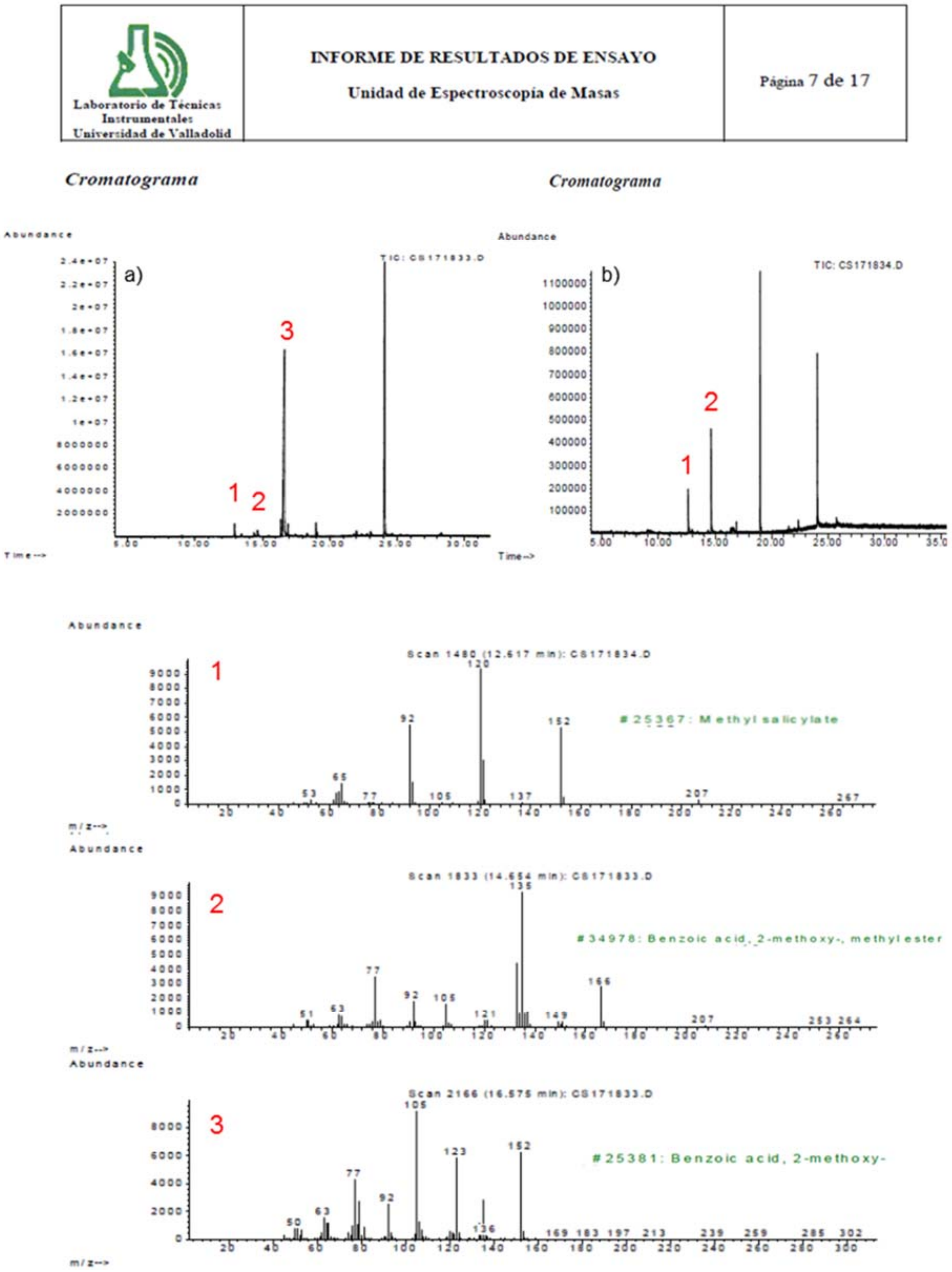


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Figure S6. CP-FTMW spectra showing all the species observed: methyl-2-methoxybenzoate (M2M), methyl salicylate (MSal), salicylic acid (Sal) and all the conformers of the *ortho*-anisic acid monomer and its T1-w-1 water complex.

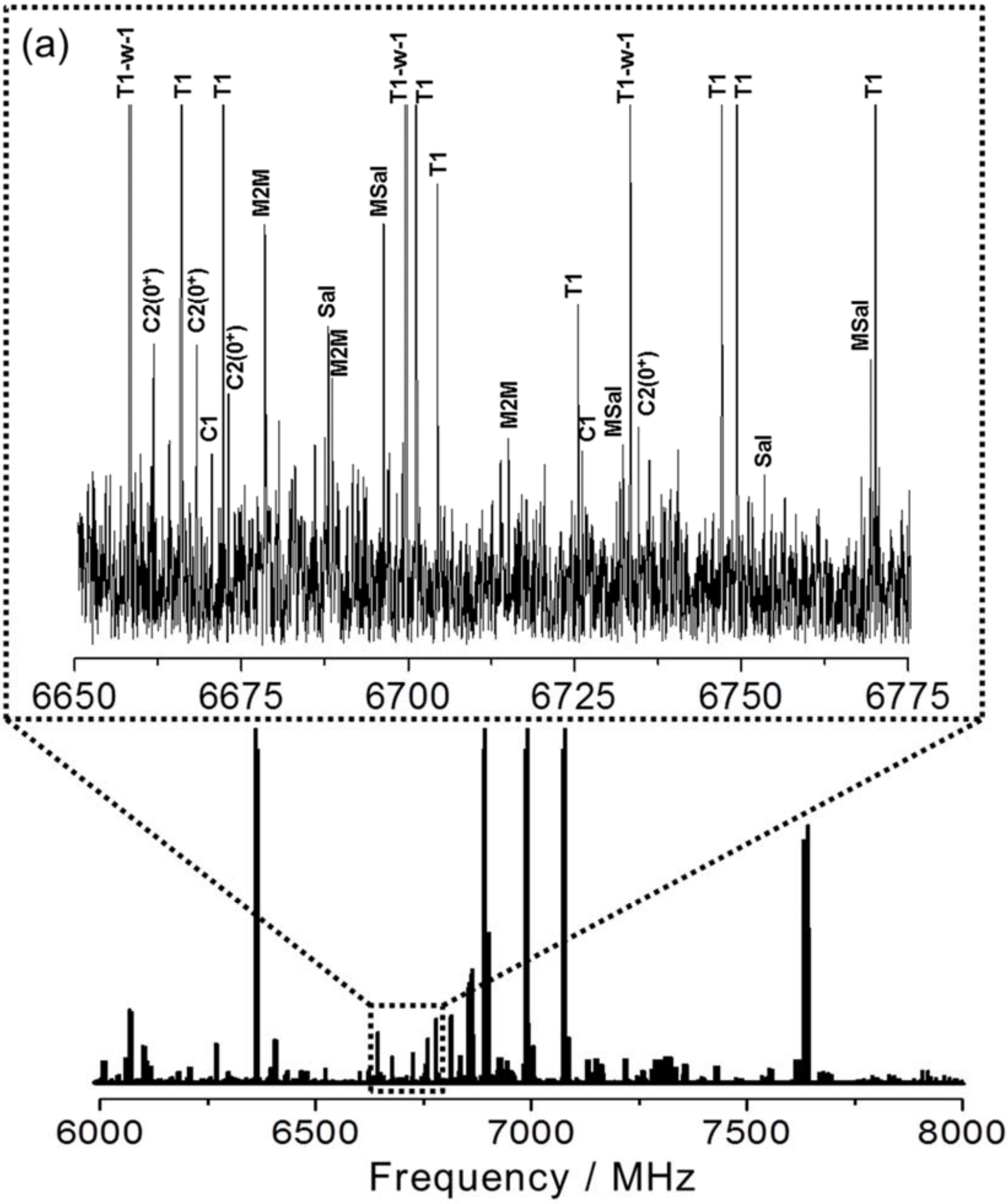

Table S1. Rotational parameters predicted at MP2/6-311++G(d,p) level of theory for the *o*-anisic acid conformers shown in Figure S1.

Parameter[a]	**T1**	**T2**	**C1**	**C2**	**C3**
A/MHz	1385.37	1434.78	1394.07	1391.70	1449.93
B/MHz	1169.37	1157.33	1132.35	1135.91	1150.50
C/MHz	638.84	672.42	649.72	655.61	680.73
P_{aa}/uÅ^2	429.24	418.01	430.81	426.31	416.56
P_{bb}/uÅ^2	361.85	333.57	347.03	344.54	325.85
P_{cc}/uÅ^2	2.94	18.66	15.49	18.60	22.71
μ_a/D	-6.57	-4.43	-2.12	-2.71	-1.48
μ_b/D	1.41	3.79	0.70	1.54	0.55
μ_c/D	0.40	0.69	0.66	0.72	0.90
E/h	-534.036897	-534.0362975	-534.034988	-534.034939	-534.0346267
ΔE_{MP2}/cm^{-1}	0.0	131.6	419.0	429.6	498.3
ΔE_{MP2}+ZPE/cm^{-1}	0.0	178.6	332.5	336.9	424.2
ΔG_{298K}/cm^{-1}	0.0	205.9	256.3	215.7	399.9

Parameter	**C4**	**C5**	**C6**	**T3**	**T4**
A/MHz	1452.80	1555.94	1585.25	1382.96	1613.30
B/MHz	1147.07	1094.29	1091.80	1107.73	1062.21
C/MHz	681.70	704.07	694.61	674.32	705.23
P_{aa}/uÅ^2	417.03	427.41	435.83	420.13	438.90
P_{bb}/uÅ^2	324.32	290.38	291.74	329.33	277.72
P_{cc}/uÅ^2	23.55	34.42	27.06	36.10	35.54
μ_a/D	-1.17	-0.68	-0.50	4.76	2.82
μ_b/D	1.86	1.09	0.88	-0.93	0.17
μ_c/D	1.83	0.53	1.64	2.03	2.92
E/h	-534.0340551	-534.032886	-534.0328471	-534.0279495	-534.0254981
ΔE_{MP2}/cm^{-1}	623.6	880.3	888.6	1963.7	2501.8
ΔE_{MP2}+ZPE/cm^{-1}	556.1	841.0	890.6	1808.9	2470.2
ΔG_{298K}/cm^{-1}	522.8	822.6	955.1	1620.2	2528.6

[a] A, B and C are the rotational constants. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia as for example $P_{cc}=(I_a+I_b-I_c)/2$. μ_a, μ_b and μ_c are the components of the electric dipole moment. E is the calculated energy and ΔE the energy relative to conformer T1. ZPE is the zero point correction energy. ΔG is the Gibbs energy relative to that of the most stable form calculated at 298K.

Table S2. Rotational parameters predicted at MP2/6-311++G(d,p) level of theory for the stable *o*-anisic acid water complex conformations shown in Figure S2.

Parameter[a]	**C1-w-1**	**C1-w-2**	**C2-w-1**	**C2-w-2**
A/MHz	1382.56	1382.62	1381.50	1382.11
B/MHz	605.39	605.99	609.03	609.66
C/MHz	433.04	433.20	436.39	436.60
P_{cc}/uÅ^2	16.64	16.44	18.77	18.54
μ_a/D	1.65	1.53	1.62	0.60
μ_b/D	1.64	0.37	1.72	1.00
μ_c/D	0.97	-1.01	1.00	2.00
E/h	-610.326934	-610.3268464	-610.3266674	-610.3266013
ΔE/cm^{-1}	0.0	19.2	58.5	73.0
Parameter	**C1-w-3**	**C1-w-4**	**T2-w-1**	**T1-w-1**
A/MHz	978.64	1102.57	1073.98	1245.93
B/MHz	901.88	792.80	827.57	663.23
C/MHz	566.10	489.77	655.10	435.70
P_{cc}/uÅ^2	92.02	31.98	154.90	3.85
μ_a/D	1.51	-2.27	1.28	6.03
μ_b/D	-0.06	0.03	-4.91	1.70
μ_c/D	-0.01	0.29	0.30	-0.49
E/h	-610.3245965	-610.3244976	-610.3236414	-610.3234613
ΔE/cm^{-1}	513.0	534.7	722.6	762.2
Parameter	**T1-w-2**	**T1-w-3**	**T1-w-4**	**C2-w-3**
A/MHz	1169.70	1359.58	991.19	963.28
B/MHz	786.10	575.85	922.36	900.34
C/MHz	570.78	409.97	621.21	574.51
P_{cc}/uÅ^2	94.77	8.31	122.12	103.15
μ_a/D	-3.26	-9.19	5.21	0.02
μ_b/D	2.59	2.97	-0.89	-1.34
μ_c/D	1.03	0.19	1.28	0.79
E/h	-610.3232456	-610.322576	-610.3224562	-610.3223874
ΔE/cm^{-1}	809.5	956.5	982.8	997.9
Parameter	**T1-w-5**	**T2-w-2**	**C2-w-4**	**T1-w-6**
A/MHz	1216.92	998.84	1220.49	1327.40
B/MHz	714.64	900.94	667.79	588.19
C/MHz	454.04	644.12	448.44	413.69
P_{cc}/uÅ^2	4.70	141.15	21.95	9.15
μ_a/D	0.02	-5.62	3.40	9.35
μ_b/D	-5.04	2.54	-0.41	1.01
μ_c/D	1.21	3.72	-0.98	0.52
E/h	-610.3219863	-610.3218824	-610.3203868	-610.3196538
ΔE/cm^{-1}	1085.9	1108.7	1436.9	1597.8

[a] A, B and C are the rotational constants. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia as for example $P_{cc}=(I_a+I_b-I_c)/2$. μ_a, μ_b and μ_c are the components of the electric dipole moment. E is the calculated energy and ΔE the energy relative to conformer C1-w-1.

Table S3. Comparison of the experimental rotational parameters of T1, C2(0^+) and C1 conformers of *o*-anisic acid with the predicted at the MP2 and CCSD and DFT B3LYP-D3 methods with the 6-311++G(d,p) (6-G) and aug-cc-pVDZ (aug) basis sets.

Parameter[a]	**T1 Exp.**	**T1 DFT/6-G**	**T1 MP2/6-G**	**T1 MP2/aug**	**T1 CCSD/6-G**
A/MHz	1387.631149(48)[b]	1379.74	1385.37	1373.50	1384.98
B/MHz	1172.426068(43)	1171.38	1169.37	1155.06	1165.75
C/MHz	638.664972(40)	636.11	638.84	630.00	635.56
P_{cc}/uÅ^2	1.975701(39)	1.62	2.94	1.65	1.62
μ_a/D		-6.92	-6.57	-6.56	-6.60
μ_b/D		1.42	1.41	1.27	1.41
μ_c/D		0.00	0.40	0.00	0.36
ΔE/cm^{-1}		0.0	0.0	0.0	0.0
Parameter[a]	**C2(0^+) Exp.**	**C2 DFT/6-G**	**C2 MP2/6-G**	**T1 MP2/aug**	**C2 CCSD/6-G**
A/MHz	1397.17908(17)	1390.58	1391.70	1381.79	1391.70
B/MHz	1155.97828(11)	1153.40	1135.91	1135.97	1135.91
C/MHz	640.89394(10)	638.60	655.61	637.11	655.61
P_{cc}/uÅ^2	5.17393(10)	5.10	18.60	8.70	18.60
μ_a/D		-3.36	-2.71	2.97	-2.81
μ_b/D		1.57	1.54	1.48	1.51
μ_c/D		0.35	0.72	-0.49	0.73
ΔE/cm^{-1}		768.6	429.6	708.8	346.5
Parameter[a]	**C1 Exp.**	**C1 DFT/6-G**	**C1 MP2/6-G**	**C1 MP2/aug**	**C1 CCSD/6-G**
A/MHz	1404.22981(39)	1398.41	1394.07	1385.85	1394.90
B/MHz	1145.60774(30)	1142.68	1132.35	1126.43	1131.61
C/MHz	638.99426(13)	635.68	649.72	636.11	646.76
P_{cc}/uÅ^2	5.07249(19)	4.32	15.49	9.42	13.75
μ_a/D		-2.39	-2.12	-2.15	-2.14
μ_b/D		1.18	0.70	0.93	0.90
μ_c/D		0.28	0.66	0.50	0.63
ΔE/cm^{-1}		850.7	419.0	737.2	386.5

[a] A, B and C are the rotational constants. P_{cc} is the planar moment of inertia in the *ab* plane, derived from $P_{cc}=(I_a+I_b-I_c)/2$. μ_a, μ_b and μ_c are the components of the electric dipole moment. ΔE is the predicted energy relative to *o*-anisic acid T1 conformer.

[b] Standard error is given in parentheses in units of the last digits.

Table S4. Comparison of the experimental rotational parameters of T1-w-1 and C2-w-1 conformers of *o*-anisic acid water complexes with the predicted at MP2 and DFT B3LYP-D3 methods with the 6-311++G(d,p) basis set.

Parameter[a]	**T1-w-1 Exp.**	**T1-w-1 DFT**	**T1-w-1 MP2**
A/MHz	1255.08080(16)[b]	1249.45	1245.93
B/MHz	656.263660(55)	665.56	663.23
C/MHz	432.826830(49)	435.63	435.70
P_{cc}/uÅ^2	2.56390(12)	1.85	3.85
μ_a/D		-6.70	6.03
μ_b/D		1.52	1.70
μ_c/D		0.84	-0.49
ΔE/cm^{-1}		523.3	722.6
Parameter[a]	**C2-w-1 Exp.**	**C2-w-1 DFT**	**C2-w-1 MP2**
A/MHz	1384.48829(73)	1377.57	1381.50
B/MHz	610.48530(30)	612.78	609.03
C/MHz	428.58680(12)	427.72	436.39
P_{cc}/uÅ^2	6.84282(46)	5.01	18.77
μ_a/D		2.40	1.62
μ_b/D		1.42	1.72
μ_c/D		1.22	1.00
ΔE/cm^{-1}		0.0	58.5
Parameter[a]		**C1-w-1 DFT**	**C1-w-1 MP2**
A/MHz		1377.58	1382.56
B/MHz		610.57	605.39
C/MHz		426.38	433.04
P_{cc}/uÅ^2		4.65	16.64
μ_a/D		2.37	1.65
μ_b/D		0.61	1.64
μ_c/D		-1.26	0.97
ΔE/cm^{-1}		54.8	0.0

[a] *A*, *B* and *C* are the rotational constants. P_{cc} is the planar moment of inertia in the *ab* plane, derived from $P_{cc}=(I_a+I_b-I_c)/2$. μ_a, μ_b and μ_c are the components of the electric dipole moment. ΔE is the predicted energy relative to *o*-anisic acid-water most stable complex.

[b] Standard error is given in parentheses in units of the last digits.

Table S5. Experimental rotational parameters for the parent *o*-anisic acid conformers.

Fitted Parameters[a]	**T1**	**C2(0^+)**	**C1**	**C2(0^-)**
A/MHz	1387.631149(48)[b]	1397.17908(17)	1404.22981(39)	1396.55339(66)
B/MHz	1172.426068(43)	1155.97828(11)	1145.60774(30)	1154.40677(30)
C/MHz	638.664972(40)	640.89394(10)	638.99426(13)	642.75248(17)
Δ_J/KHz	0.05698(43)	0.0670(16)	0.0467(25)	0.0211(19)
Δ_{JK}/KHz	-0.08210(37)	-0.0396(18)	-	-
Δ_K/KHz	0.03139(52)	-	-	-
δ_J/KHz	-0.001822(52)	0.00141(37)	0.0111(14)	-
δ_K/KHz	-0.02248(57)	-0.02185(27)	0.0875(72)	-0.103(19)
N	256	105	48	25
σ/KHz	4.5	4.7	4.6	4.1
Derived Parameters				
P_{aa}/uÅ^2	429.078352(39)	432.01336(10)	436.07241(19)	431.08984(25)
P_{bb}/uÅ^2	362.226997(39)	356.53991(10)	354.82516(19)	355.18330(25)
P_{cc}/uÅ^2	1.975701(39)	5.17393(10)	5.07249(19)	6.69260(25)

[a] A, B and C are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. N is the number of rotational transitions fitted. σ is the rms deviations of the fit. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia as for example $P_{cc}=(I_a+I_b-I_c)/2$.

[b] Standard error is given in parentheses in units of the last digits.

Table S6. Experimental rotational parameters for the observed isotopologues of the *o*-anisic acid conformers. See Figure 3 for atom labeling.

Fitted Parameters[a]	**T1 $^{13}C_1$**	**T1 $^{13}C_2$**	**T1 $^{13}C_3$**	**T1 $^{13}C_4$**	**T1 $^{13}C_5$**	**T1 $^{13}C_6$**
A/MHz	1386.83142(30)[b]	1387.00859(34)	1387.64670(33)	1380.47188(33)	1367.75951(40)	1374.88581(32)
B/MHz	1172.04484(10)	1171.18408(11)	1161.72917(11)	1158.70791(17)	1168.44063(16)	1172.39140(11)
C/MHz	638.383574(42)	638.165371(49)	635.482020(47)	633.070981(36)	633.253841(57)	635.941960(46)
Δ_J/KHz	[0.05698][c]	[0.05698]	[0.05698]	[0.05698]	[0.05698]	[0.05698]
Δ_{JK}/KHz	[-0.08210]	[-0.08210]	[-0.08210]	[-0.08210]	[-0.08210]	[-0.08210]
Δ_K/KHz	[0.03139]	[0.03139]	[0.03139]	[0.03139]	[0.03139]	[0.03139]
δ_J/KHz	[-0.001822]	[-0.001822]	[-0.001822]	[-0.001822]	[-0.001822]	[-0.001822]
δ_K/KHz	[-0.02248]	[-0.02248]	[-0.02248]	[-0.02248]	[-0.02248]	[-0.02248]
N	32	30	34	37	32	31
σ/KHz	4.4	4.9	4.2	4.2	2.4	3.2
Derived Parameters						
P_{aa}/uÅ^2	429.217849(84)	429.53492(10)	433.046623(93)	434.18162(10)	430.54865(12)	429.090754(92)
P_{bb}/uÅ^2	362.436307(84)	362.38992(10)	362.222154(93)	364.11592(10)	367.51837(12)	365.602851(92)
P_{cc}/uÅ^2	1.976413(84)	1.97625(10)	1.976463(93)	1.97576(10)	1.97568(12)	1.976046(92)

[a] A, B and C are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. N is the number of rotational transitions fitted. σ is the rms deviations of the fit. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia as for example $P_{cc}=(I_a+I_b-I_c)/2$.

[b] Standard error is given in parentheses in units of the last digits.

[c] Parameters in square brackets were kept fixed as those given for the parent species in the fit.

Table S6 (Continued).

Fitted Parameters[a]	**T1 $^{13}C_{11}$**	**T1 $^{13}C_{16}$**	**T1 $^{2}D_{15}$**	**T1 $^{18}O_{12}$**	**C2(0^{+}) $^{2}D_{15}$**
A/MHz	1387.62832(31)	1361.37965(34)	1376.42981(20)	1364.67665(47)	1391.3870(11)
B/MHz	1163.15603(10)	1165.97364(15)	1167.36958(19)	1171.49441(38)	1131.33991(65)
C/MHz	635.903443(42)	631.161638(51)	634.79547(18)	633.494683(99)	631.74216(22)
Δ_J/KHz	[0.05698][c]	[0.05698]	[0.05698]	[0.05698]	[0.0670]
Δ_{JK}/KHz	[-0.08210]	[-0.08210]	[-0.08210]	[-0.08210]	[-0.0396]
Δ_K/KHz	[0.03139]	[0.03139]	[0.03139]	[0.03139]	-
δ_J/KHz	[-0.001822]	[-0.001822]	[-0.001822]	[-0.001822]	[0.00141]
δ_K/KHz	[-0.02248]	[-0.02248]	[-0.02248]	[-0.02248]	[-0.2185]
N	33	33	83	17	20
σ/KHz	4.1	3.3	6.7	7.9	6.6
Derived Parameters					
P_{aa}/uÅ^2	432.513868(86)	431.46318(11)	430.94175(17)	429.41586(20)	441.73274(41)
P_{bb}/uÅ^2	362.227872(86)	369.24932(11)	365.18714(17)	368.34776(20)	358.24396(41)
P_{cc}/uÅ^2	1.975569(86)	1.97631(11)	1.97943(17)	1.98100(20)	4.97563(41)

[a] A, B and C are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. N is the number of rotational transitions fitted. σ is the rms deviations of the fit. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia as for example $P_{cc}=(I_a+I_b-I_c)/2$.

[b] Standard error is given in parentheses in units of the last digits.

[c] Parameters in square brackets were kept fixed as those given for the parent species in the fit.

Table S7. Spectroscopic parameters determined for the parent T1-w-1 and C2-w-1 conformations of *o*-anisic acid-water complex.

Fitted Parameters[a]	**T1-w-1**	**C2-w-1**
A/MHz	1255.08080(16)[b]	1384.48829(73)
B/MHz	656.263660(55)	610.48530(30)
C/MHz	432.826830(49)	428.58680(12)
Δ_J/KHz	0.0868(29)	0.0475(27)
Δ_{JK}/KHz	-0.1493(91)	-
Δ_K/KHz	0.0787(61)	-0.0352(27)
δ_J/KHz	0.0071(16)	-
δ_K/KHz	0.0236(43)	-0.0204(46)
N	149	46
σ/KHz	4.0	5.5
Derived Parameters		
P_{aa}/uÅ^2	767.52142(12)	820.98876(46)
P_{bb}/uÅ^2	400.10261(12)	358.18664(46)
P_{cc}/uÅ^2	2.56390(12)	6.84282(46)

[a] A, B and C are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. N is the number of rotational transitions fitted. σ is the rms deviations of the fit. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia as for example $P_{cc}=(I_a+I_b-I_c)/2$.

[b] Standard error is given in parentheses in units of the last digits.

Table S8. Experimental rotational parameters for the observed isotopologues of the *o*-anisic acid-water complex T1-w-1. See Figure 3 for atom labeling.

Fitted Parameterrs[a]	**$^{2}D_{15}$**	**$^{2}D_{20}$**	**$^{18}O_{21}$**	**$^{2}D_{15}$-$^{2}D_{20}$**	**$^{2}D_{20}$-$^{2}D_{22}$**	**$^{2}D_{15}$-$^{2}D_{20}$-$^{2}D_{22}$**
A/MHz	1240.05696(96)[b]	1254.75992(37)	1253.9057(11)	1239.79159(58)	1254.28123(47)	1239.27646(44)
B/MHz	655.70387(21)	645.56458(18)	626.72729(15)	645.00403(17)	625.48016(16)	624.90712(16)
C/MHz	430.78530(16)	428.11656(14)	419.652182(38)	426.10839(13)	419.19797(11)	417.25576(12)
Δ_J/KHz	[0.0868(29)][c]	[0.0868(29)]	[0.0868(29)]	[0.0868(29)]	[0.0868(29)]	[0.0868(29)]
Δ_{JK}/KHz	[-0.1493(91)]	[-0.1493(91)]	[-0.1493(91)]	[-0.1493(91)]	[-0.1493(91)]	[-0.1493(91)]
Δ_K/KHz	[0.0787(61)]	[0.0787(61)]	[0.0787(61)]	[0.0787(61)]	[0.0787(61)]	[0.0787(61)]
δ_J/KHz	[0.0071(16)]	[0.0071(16)]	[0.0071(16)]	[0.0071(16)]	[0.0071(16)]	[0.0071(16)]
δ_K/KHz	[0.0236(43)]	[0.0236(43)]	[0.0236(43)]	[0.0236(43)]	[0.0236(43)]	[0.0236(43)]
N	33	45	21	41	46	37
σ/KHz	7.8	5.4	1.4	7.7	6.8	7.6
Derived Parameters						
P_{aa}/uÅ^2	768.17763(50)	780.27461(36)	803.80732(33)	780.96508(38)	805.32400(34)	806.06042(35)
P_{bb}/uÅ^2	404.97987(34)	400.19599(30)	400.47334(15)	405.06885(28)	400.26153(26)	405.13678(28)
P_{cc}/uÅ^2	2.56512(22)	2.57350(19)	2.570532(54)	2.56337(18)	2.66167(16)	2.66488(17)

[a] A, B and C are the rotational constants. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. N is the number of rotational transitions fitted. σ is the rms deviations of the fit. $P_{\alpha\alpha}$ (α= a, b or c) are the planar moments of inertia derived from the moments of inertia as for example $P_{cc}=(I_a+I_b-I_c)/2$.

[b] Standard error is given in parentheses in units of the last digits.

[c] Parameters in square brackets were kept fixed as those given for the parent species in the fit.

Table S9. Observed rotational transitions and residuals (in MHz) for the T1 conformer of *o*-anisic acid in the ground vibrational state.

J'	**K_{-1}'**	**K_{+1}'**	**J''**	**K_{-1}''**	**K_{+1}''**	**Obs.**	**Obs.-Cal.**
2	1	2	1	1	1	3088.4211	0.0005
2	0	2	1	0	1	3250.5653	0.0001
2	1	1	1	1	0	4155.9417	-0.0002
2	2	0	1	0	1	5922.1360	-0.0030
3	1	3	2	1	2	4443.4419	0.0002
3	0	3	2	0	2	4488.0203	-0.0001
3	1	2	2	1	1	5831.8774	-0.0006
3	2	1	2	0	2	9050.0919	-0.0018
3	2	1	2	2	0	6378.5193	-0.0005
3	2	2	2	2	1	5433.2719	0.0017
3	3	0	2	1	1	8891.3432	0.0001
3	3	0	3	1	3	6049.1819	-0.0020
3	2	1	2	1	2	8997.0310	-0.0022
3	2	2	2	1	1	6078.8823	-0.0026
3	3	0	2	2	1	8245.7295	0.0013
3	3	1	2	2	0	7661.2676	-0.0001
3	3	0	3	0	3	6057.6559	-0.0095
4	1	4	3	1	3	5738.6966	-0.0002
4	0	4	3	0	3	5746.0623	0.0018
4	1	3	3	1	2	7107.8641	-0.0006
4	2	2	3	2	1	8312.8849	-0.0005
4	2	3	3	2	2	6918.0302	-0.0006
4	3	1	3	3	0	8448.3680	-0.0001
4	3	2	3	3	1	7682.4973	-0.0003
4	1	3	4	1	4	4358.8872	0.0003
4	2	2	4	2	3	2711.7200	-0.0004
4	2	3	4	0	4	4417.1786	0.0008
4	3	2	4	1	3	3421.2526	-0.0009
4	4	0	4	2	3	6541.1110	-0.0015
4	0	4	3	1	3	5737.5784	-0.0005
4	1	4	3	0	3	5747.1778	-0.0006
4	1	3	3	2	2	6860.8573	-0.0005
4	2	2	3	3	1	7030.1343	-0.0032
4	2	3	3	1	2	7165.0377	0.0000
4	3	2	3	2	1	8965.2464	0.0008
4	4	0	4	1	3	6598.2873	0.0016
5	1	5	4	1	4	7018.8171	-0.0002

Table S9 (Continued).

J′	**K$_{-1}$′**	**K$_{+1}$′**	**J′′**	**K$_{-1}$′′**	**K$_{+1}$′′**	**Obs.**	**Obs.-Cal.**
5	0	5	4	0	4	7019.8028	0.0005
5	1	4	4	1	3	8314.2809	0.0011
5	2	3	4	2	2	9765.2089	-0.0009
5	2	3	4	4	0	5935.8289	0.0110
5	2	4	4	2	3	8266.9245	-0.0006
5	3	2	4	3	1	10652.9157	-0.0006
5	3	3	4	3	2	9324.4857	-0.0004
5	4	1	4	4	0	10381.3086	-0.0014
5	4	2	4	4	1	9843.9564	0.0000
5	1	4	5	1	5	5654.3508	0.0016
5	2	3	5	2	4	4210.0047	-0.0005
5	2	4	5	0	5	5664.3012	0.0006
5	3	2	5	3	3	2307.1427	-0.0024
5	3	3	5	1	4	4431.4600	0.0000
5	4	2	5	2	3	3804.7003	0.0034
5	5	0	5	3	3	7295.0572	-0.0021
5	0	5	4	1	4	7018.6856	0.0012
5	1	5	4	0	4	7019.9352	0.0000
5	1	4	4	2	3	8257.1066	-0.0001
5	2	3	4	3	2	9112.8527	0.0028
5	2	4	4	1	3	8324.0998	0.0017
5	3	3	4	2	2	9976.8487	0.0024
5	3	3	4	4	0	6147.4408	-0.0133
6	1	6	5	1	5	8296.4203	0.0012
6	0	6	5	0	5	8296.5359	-0.0013
6	1	5	5	1	4	9568.6048	0.0002
6	2	4	5	2	3	10934.0879	-0.0001
6	2	4	5	4	1	6488.5931	-0.0027
6	2	5	5	2	4	9560.2217	0.0001
6	3	3	5	3	2	12379.3247	-0.0015
6	3	3	5	5	0	7391.4074	-0.0046
6	3	4	5	3	3	10769.4284	0.0004
6	4	2	5	4	1	12826.2081	-0.0017
6	4	3	5	4	2	11648.2233	0.0022
6	5	2	5	5	1	11932.4422	-0.0006
6	5	1	5	5	0	12252.9038	-0.0016
6	1	5	6	1	6	6926.5305	-0.0041
6	2	4	6	2	5	5583.8716	-0.0001

Table S9 (Continued).

J′	**K_{-1}′**	**K_{+1}′**	**J″**	**K_{-1}″**	**K_{+1}″**	**Obs.**	**Obs.-Cal.**
6	3	3	6	3	4	3917.0432	-0.0001
6	3	4	6	1	5	5632.2801	-0.0033
6	4	3	6	2	4	4518.8296	-0.0003
6	5	1	6	3	4	8778.5375	0.0007
6	5	2	6	3	3	4496.1310	0.0013
6	6	0	6	4	3	8287.8629	-0.0014
6	6	1	6	4	2	6450.9504	-0.0013
6	1	5	5	2	4	9558.7872	0.0009
6	2	5	5	1	4	9570.0400	0.0000
6	3	4	5	4	1	6535.5661	-0.0059
7	1	7	6	1	6	9573.7191	-0.0003
7	0	7	6	0	6	9573.7337	0.0009
7	1	6	6	1	5	10840.8648	-0.0005
7	2	5	6	2	4	12136.8690	0.0017
7	2	6	6	2	5	10839.6192	-0.0006
7	3	4	6	5	1	8759.0289	0.0001
7	3	5	6	3	4	12098.2416	0.0000
7	1	6	7	1	7	8193.6828	0.0022
7	2	6	7	0	7	8193.8695	-0.0025
7	3	4	7	3	5	5439.3236	-0.0003
7	3	5	7	1	6	6889.6600	0.0003
7	4	3	7	4	4	3459.3255	0.0007
7	4	4	7	2	5	5607.4743	-0.0024
7	5	3	7	3	4	4759.2674	-0.0007
7	6	2	7	4	3	5552.5553	0.0008
7	1	6	6	2	5	10839.4303	0.0003
7	2	5	6	3	4	12089.8923	0.0013
7	2	6	6	1	5	10841.0557	0.0004
7	4	4	6	5	1	8918.8289	-0.0020
7	2	5	7	1	6	6881.3096	0.0006
7	3	4	7	2	5	5447.6770	0.0024
7	3	5	7	2	6	6889.4689	-0.0008
7	4	4	7	3	5	5599.1273	0.0012
8	1	8	7	1	7	10851.0080	0.0012
8	0	8	7	0	7	10851.0080	0.0012
8	1	7	7	1	6	12116.9243	0.0004
8	2	7	7	2	6	12116.7577	0.0002
8	3	5	7	5	2	8684.2961	-0.0021

Table S9 (Continued).

J'	**K_{-1}'**	**K_{+1}'**	**J''**	**K_{-1}''**	**K_{+1}''**	**Obs.**	**Obs.-Cal.**
8	1	7	8	1	8	9459.5959	-0.0024
8	2	6	8	2	7	8156.5006	0.0020
8	2	7	8	0	8	9459.6223	0.0003
8	3	5	8	3	6	6803.0630	-0.0022
8	3	6	8	1	7	8157.8200	0.0010
8	4	4	8	4	5	5165.8326	0.0000
8	4	5	8	2	6	6838.8607	-0.0015
8	5	3	8	5	4	2867.9297	0.0002
8	5	4	8	3	5	5624.8977	0.0092
8	6	3	8	4	4	5257.6567	0.0016
8	7	1	8	5	4	9913.2139	0.0030
8	7	2	8	5	3	6960.5965	0.0000
8	3	5	8	2	6	6804.3590	-0.0031
8	4	4	8	3	5	5200.3297	-0.0030
8	4	5	8	3	6	6837.5640	-0.0013
8	5	4	8	4	5	5590.3735	-0.0148
8	6	3	8	5	4	4833.0989	-0.0004
8	7	2	8	6	3	4995.4263	-0.0002
9	1	9	8	1	8	12128.3024	-0.0006
9	0	9	8	0	8	12128.3024	-0.0006
9	3	6	8	5	3	7467.3193	0.0007
9	2	7	9	2	8	9426.2367	0.0007
9	3	6	9	3	7	8100.8333	0.0004
9	3	7	9	1	8	9426.4226	0.0001
9	4	5	9	4	6	6665.5141	-0.0024
9	4	6	9	2	7	8107.2735	-0.0020
9	5	4	9	5	5	4714.6741	0.0031
9	5	5	9	3	6	6784.1220	-0.0016
9	6	3	9	6	4	2205.5120	0.0097
9	6	4	9	4	5	5747.3631	0.0006
9	7	3	9	5	4	6110.3530	0.0000
9	4	5	9	3	6	6671.7740	-0.0015
9	4	6	9	3	7	8107.0927	0.0008
9	5	4	9	4	5	4827.0086	-0.0104
9	5	5	9	4	6	6777.8624	-0.0022
9	6	4	9	5	5	5635.0113	-0.0030
9	7	3	9	6	4	5190.0051	-0.0045
9	8	1	9	7	2	5227.4268	0.0077

Table S9 (Continued).

J´	**K$_{-1}$´**	**K$_{+1}$´**	**J´´**	**K$_{-1}$´´**	**K$_{+1}$´´**	**Obs.**	**Obs.-Cal.**
9	8	2	9	7	3	5668.4916	0.0018
9	9	0	9	8	1	6588.0896	-0.0059
9	9	1	9	8	2	6623.6298	-0.0103
10	3	7	10	3	8	9379.5887	0.0005
10	4	6	10	4	7	8016.6051	0.0001
10	4	7	10	2	8	9380.6237	-0.0004
10	5	5	10	5	6	6422.4741	-0.0010
10	5	6	10	3	7	8041.4286	0.0001
10	6	4	10	6	5	4082.3504	-0.0001
10	6	5	10	4	6	6748.8641	-0.0014
10	7	4	10	5	5	6068.4945	-0.0009
10	8	3	10	6	4	7355.9234	0.0006
10	4	6	10	3	7	8017.6109	-0.0056
10	5	5	10	4	6	6446.2875	0.0004
10	5	6	10	4	7	8040.4102	-0.0065
10	6	5	10	5	6	6725.0518	-0.0018
10	7	3	10	6	4	3232.8140	0.0134
10	7	4	10	6	5	5765.9115	-0.0053
10	8	2	10	7	3	4368.6943	0.0159
10	8	3	10	7	4	5672.3548	-0.0017
10	9	1	10	8	2	6174.7204	-0.0007
10	9	2	10	8	3	6405.2745	-0.0021
10	10	1	10	9	2	7424.5228	0.0045
11	4	7	11	4	8	9315.1313	0.0014
11	5	6	11	5	7	7884.6304	-0.0002
11	5	7	11	3	8	9319.6591	0.0001
11	6	5	11	6	6	6015.0909	-0.0014
11	6	6	11	4	7	7964.4930	-0.0008
11	7	4	11	7	5	3318.7105	0.0149
11	7	5	11	5	6	6779.4479	-0.0010
11	8	4	11	6	5	6699.2074	-0.0007
11	4	7	11	3	8	9315.2826	0.0024
11	5	6	11	4	7	7889.0044	-0.0050
11	5	7	11	4	8	9319.5088	0.0003
11	6	5	11	5	6	6090.5750	-0.0017
11	6	6	11	5	7	7960.1201	0.0049
11	7	4	11	6	5	4007.5794	0.0117
11	7	5	11	6	6	6703.9664	0.0019

Table S9 (Continued).

J´	K_{-1}´	K_{+1}´	J´´	K_{-1}´´	K_{+1}´´	Obs.	Obs.-Cal.
11	8	4	11	7	5	6010.3348	-0.0012
11	9	2	11	8	3	5403.5323	0.0032
11	9	3	11	8	4	6267.5782	-0.0009
11	10	1	11	9	2	7070.9304	0.0060
11	10	2	11	9	3	7181.5936	-0.0052
12	5	7	12	5	8	9225.3726	-0.0006
12	6	6	12	6	7	7669.9186	-0.0016
12	6	7	12	4	8	9241.8995	0.0003
12	7	5	12	7	6	5403.3382	-0.0069
12	7	6	12	5	7	7891.0818	0.0009
12	8	5	12	6	6	6951.9595	0.0000
12	9	4	12	7	5	7726.4137	0.0004
12	5	7	12	4	8	9226.1022	0.0010
12	6	6	12	5	7	7685.7131	-0.0050
12	6	7	12	5	8	9241.1710	-0.0001
12	7	5	12	6	6	5608.6881	-0.0197
12	7	6	12	6	7	7875.2782	-0.0047
12	8	5	12	7	6	6746.6020	0.0053
12	9	3	12	8	4	4438.3696	-0.0036
12	9	4	12	8	5	6383.1728	0.0111
12	10	2	12	9	3	6446.1640	-0.0141
12	10	3	12	9	4	6952.7076	0.0122
12	11	1	12	10	2	7929.3498	-0.0061
12	11	2	12	10	3	7979.3111	-0.0088
13	6	7	13	6	8	9096.6488	0.0006
13	7	6	13	7	7	7318.2383	-0.0011
13	7	7	13	5	8	9148.7504	0.0008
13	8	5	13	8	6	4601.8111	-0.0026
13	8	6	13	6	7	7853.4666	0.0008
13	9	5	13	7	6	7371.5122	-0.0007
13	10	4	13	8	5	9167.4631	-0.0034
13	8	5	13	7	6	5087.8786	0.0067
13	8	6	13	7	7	7804.3094	0.0117
13	9	4	13	8	5	4012.4610	-0.0011
13	9	5	13	8	6	6885.4500	-0.0048
13	10	3	13	9	4	5445.7811	0.0182
13	10	4	13	9	5	6883.8134	-0.0120

Table S9 (Continued).

J´	K_{-1}´	K_{+1}´	J´´	K_{-1}´´	K_{+1}´´	Obs.	Obs.-Cal.
13	11	2	13	10	3	7432.6277	-0.0044
13	11	3	13	10	4	7700.9726	0.0020
14	7	7	14	7	8	8903.6149	-0.0018
14	8	6	14	8	7	6769.6929	0.0022
14	8	7	14	6	8	9048.5166	-0.0001
14	9	6	14	7	7	7909.5076	-0.0038
14	9	5	14	8	6	4683.5346	-0.0134
14	9	6	14	8	7	7774.8101	0.0006
14	10	4	14	9	5	4549.4123	-0.0085
14	10	5	14	9	6	7145.7499	0.0098
14	11	3	14	10	4	6556.3678	-0.0057
14	11	4	14	10	5	7497.4193	-0.0088
15	8	7	15	8	8	8602.8965	0.0010
15	9	6	15	9	7	5996.0453	-0.0061
15	9	7	15	7	8	8962.3563	0.0011
15	11	5	15	9	6	9363.2135	0.0011
15	8	7	15	7	8	8634.2116	-0.0006
15	9	6	15	8	7	6324.1962	0.0018
15	10	6	15	9	7	7819.9170	0.0060
15	11	5	15	10	6	7539.3520	-0.0007
15	12	3	15	11	4	7649.1372	0.0003
16	11	6	16	9	7	8683.5005	-0.0022
16	11	6	16	10	7	7971.2520	0.0054
16	12	4	16	11	5	6529.3722	0.0012
17	10	7	17	10	8	7437.4185	-0.0018
17	11	7	17	10	8	9026.5826	0.0025
17	9	8	17	10	8	9883.4599	-0.0025
17	10	7	17	9	8	7651.9241	0.0025
17	14	4	17	13	5	9763.9258	0.0009
18	11	7	18	11	8	6501.5385	-0.0094

Table S10. Observed rotational transitions and residuals (in MHz) for $^{13}C_1$ isotopomer of the T1 *o*-anisic acid conformer in the ground vibrational state. See Figure 3 for atom labeling.

J′	**K_{-1}'**	**K_{+1}'**	**J′′**	**K_{-1}''**	**K_{+1}''**	**Obs.**	**Obs.-Cal.**
3	1	2	2	1	1	5829.4269	0.0092
3	2	1	2	2	0	6376.5783	-0.0030
4	1	4	3	1	3	5736.1795	-0.0025
4	0	4	3	0	3	5743.5093	-0.0022
4	1	3	3	1	2	7104.5340	0.0012
4	2	2	3	2	1	8309.7372	0.0001
4	2	3	3	2	2	6915.2100	-0.0010
4	3	1	3	3	0	8446.1985	-0.0010
4	3	2	3	3	1	7679.9118	0.0006
5	1	5	4	1	4	7015.7273	0.0002
5	0	5	4	0	4	7016.7050	-0.0009
5	1	4	4	1	3	8310.5032	-0.0002
5	2	3	4	2	2	9760.6899	-0.0007
5	2	4	4	2	3	8263.3573	-0.0006
5	3	3	4	3	2	9320.9233	0.0000
5	4	2	4	4	1	9840.8988	0.0016
5	1	5	4	0	4	7016.8483	0.0103
6	1	6	5	1	5	8292.7642	0.0001
6	0	6	5	0	5	8292.8811	-0.0001
6	1	5	5	1	4	9564.3564	0.0006
6	2	5	5	2	4	9556.0222	-0.0009
6	1	5	6	1	6	6923.5759	-0.0028
6	2	5	6	0	6	6925.0291	0.0114
7	1	7	6	1	6	9569.4995	-0.0019
7	0	7	6	0	6	9569.5160	0.0013
7	1	6	6	1	5	10836.0819	0.0022
7	3	5	7	1	6	6886.8011	-0.0106
8	1	8	7	1	7	10846.2257	-0.0004
8	0	8	7	0	7	10846.2257	-0.0004
8	1	7	7	1	6	12111.5832	0.0012
8	2	7	7	2	6	12111.4178	0.0007
8	4	5	8	2	6	6836.1330	-0.0105

Table S11. Observed rotational transitions and residuals (in MHz) for $^{13}\mathrm{C}_2$ isotopomer of the T1 *o*-anisic acid conformer in the ground vibrational state. See Figure 3 for atom labeling.

J´	**K$_{-1}$´**	**K$_{+1}$´**	**J´´**	**K$_{-1}$´´**	**K$_{+1}$´´**	**Obs.**	**Obs.-Cal.**
3	1	2	2	1	1	5827.0813	0.0186
3	2	1	2	2	0	6371.4301	-0.0006
4	1	4	3	1	3	5734.1800	0.0011
4	0	4	3	0	3	5741.6135	0.0015
4	1	3	3	1	2	7102.8072	0.0027
4	2	2	3	2	1	8305.1522	-0.0001
4	2	3	3	2	2	6912.0764	0.0001
4	3	1	3	3	0	8438.0120	0.0009
4	3	2	3	3	1	7674.5627	-0.0050
4	1	3	3	2	2	6854.3646	0.0159
5	1	5	4	1	4	7013.3252	-0.0005
5	0	5	4	0	4	7014.3227	-0.0009
5	1	4	4	1	3	8308.0640	-0.0007
5	2	3	4	2	2	9758.1140	-0.0018
5	2	4	4	2	3	8260.2876	0.0000
5	3	3	4	3	2	9315.8862	-0.0001
5	4	2	4	4	1	9833.1766	-0.0012
6	1	6	5	1	5	8289.9329	0.0001
6	0	6	5	0	5	8290.0513	-0.0015
6	1	5	5	1	4	9561.2101	-0.0030
6	2	5	5	2	4	9552.7233	0.0007
6	1	5	6	1	6	6920.9370	0.0055
6	2	5	6	0	6	6922.4066	0.0000
7	1	7	6	1	6	9566.2338	-0.0004
7	0	7	6	0	6	9566.2478	0.0000
7	1	6	6	1	5	10832.4206	0.0000
8	1	8	7	1	7	10842.5224	0.0002
8	0	8	7	0	7	10842.5224	0.0002
8	1	7	7	1	6	12107.4673	0.0010
8	2	7	7	2	6	12107.2981	0.0016

Table S12. Observed rotational transitions and residuals (in MHz) for $^{13}C_3$ isotopomer of the T1 *o*-anisic acid conformer in the ground vibrational state. See Figure 3 for atom labeling.

J´	K_{-1}´	K_{+1}´	J´´	K_{-1}´´	K_{+1}´´	Obs.	Obs.-Cal.
3	1	2	2	1	1	5798.6222	-0.0059
3	2	1	2	2	0	6315.3521	-0.0027
4	1	4	3	1	3	5709.6205	-0.0028
4	0	4	3	0	3	5718.1253	0.0008
4	1	3	3	1	2	7079.7519	-0.0006
4	2	2	3	2	1	8252.4385	-0.0011
4	2	3	3	2	2	6875.2611	-0.0017
4	3	1	3	3	0	8350.4121	-0.0015
4	3	2	3	3	1	7615.5511	-0.0092
4	1	3	3	2	2	6808.9875	-0.0103
5	1	5	4	1	4	6983.8001	0.0035
5	0	5	4	0	4	6984.9962	-0.0005
5	1	4	4	1	3	8277.2463	-0.0003
5	2	3	4	2	2	9723.8325	0.0005
5	2	4	4	2	3	8223.0008	0.0000
5	4	2	4	4	1	9749.0853	0.0030
5	0	5	4	1	4	6983.6147	-0.0096
5	1	5	4	0	4	6985.1691	0.0002
5	1	4	4	2	3	8210.9821	0.0003
6	1	6	5	1	5	8255.1045	-0.0008
6	0	6	5	0	5	8255.2570	-0.0002
6	1	5	5	1	4	9522.3318	-0.0006
6	2	5	5	2	4	9512.1670	-0.0001
6	1	5	6	1	6	6888.9388	-0.0013
6	2	5	6	0	6	6890.8073	-0.0067
7	1	7	6	1	6	9526.0433	-0.0023
7	0	7	6	0	6	9526.0636	0.0000
7	1	6	6	1	5	10787.3387	0.0021
7	2	5	7	2	6	6837.9044	-0.0016
8	1	8	7	1	7	10796.9658	0.0012
8	0	8	7	0	7	10796.9658	0.0012
8	1	7	7	1	6	12056.8007	0.0002
8	2	7	7	2	6	12056.5759	0.0003
9	5	5	9	3	6	6739.5997	0.0125

Table S13. Observed rotational transitions and residuals (in MHz) for $^{13}C_4$ isotopomer of the T1 *o*-anisic acid conformer in the ground vibrational state. See Figure 3 for atom labeling.

J´	**K_{-1}´**	**K_{+1}´**	**J´´**	**K_{-1}´´**	**K_{+1}´´**	**Obs.**	**Obs.-Cal.**
3	1	2	2	1	1	5777.9807	-0.0022
3	2	1	2	2	0	6300.3117	-0.0019
3	3	1	2	2	0	7621.4854	0.0082
4	1	4	3	1	3	5688.1324	-0.0004
4	0	4	3	0	3	5696.2622	0.0002
4	1	3	3	1	2	7050.9727	-0.0006
4	2	2	3	2	1	8226.7476	-0.0015
4	2	3	3	2	2	6851.6298	0.0025
4	3	2	3	3	1	7594.8108	-0.0019
4	1	3	3	2	2	6788.3266	-0.0045
4	2	3	3	1	2	7114.2768	0.0072
5	1	5	4	1	4	6957.3487	0.0016
5	0	5	4	0	4	6958.4778	0.0000
5	1	4	4	1	3	8244.6818	-0.0007
5	2	3	4	2	2	9685.2450	0.0010
5	2	4	4	2	3	8192.6942	-0.0004
5	3	3	4	3	2	9228.8341	0.0018
5	0	5	4	1	4	6957.1824	-0.0052
5	1	5	4	0	4	6958.6289	-0.0083
5	2	4	4	1	3	8255.9908	0.0000
6	1	6	5	1	5	8223.8096	-0.0009
6	0	6	5	0	5	8223.9509	-0.0005
6	1	5	5	1	4	9485.8945	-0.0011
6	2	5	5	2	4	9476.3058	0.0000
6	2	5	6	0	6	6865.7879	-0.0151
6	2	5	5	1	4	9487.6135	-0.0006
7	1	7	6	1	6	9489.9265	-0.0004
7	0	7	6	0	6	9489.9435	0.0000
7	1	6	6	1	5	10746.3677	0.0001
7	2	5	7	2	6	6814.9030	-0.0099
7	3	5	7	1	6	6825.1221	0.0006
8	1	8	7	1	7	10756.0235	-0.0012
8	0	8	7	0	7	10756.0235	-0.0012
8	1	7	7	1	6	12011.0848	0.0005
8	2	7	7	2	6	12010.8797	0.0013
8	3	5	8	3	6	6729.4082	-0.0002
8	4	5	8	2	6	6772.0562	0.0068

Table S14. Observed rotational transitions and residuals (in MHz) for $^{13}C_5$ isotopomer of the T1 *o*-anisic acid conformer in the ground vibrational state. See Figure 3 for atom labeling.

J´	K_{-1}´	K_{+1}´	J´´	K_{-1}´´	K_{+1}´´	Obs.	Obs.-Cal.
3	2	1	2	2	0	6362.7042	0.0035
4	1	4	3	1	3	5690.6656	-0.0015
4	0	4	3	0	3	5696.6980	-0.0030
4	1	3	3	1	2	7038.9007	0.0021
4	2	2	3	2	1	8264.1416	0.0001
4	2	3	3	2	2	6869.2650	0.0041
4	3	1	3	3	0	8445.0106	-0.0026
4	3	2	3	3	1	7652.5103	0.0069
4	1	3	3	2	2	6822.6400	-0.0040
5	1	5	4	1	4	6959.4692	-0.0008
5	0	5	4	0	4	6960.2221	-0.0012
5	1	4	4	1	3	8239.2287	0.0003
5	2	3	4	2	2	9672.1016	-0.0048
5	2	4	4	2	3	8200.0808	0.0013
5	3	3	4	3	2	9269.0362	0.0036
6	1	6	5	1	5	8226.1721	-0.0006
6	0	6	5	0	5	8226.2548	-0.0023
6	1	5	5	1	4	9486.2996	0.0000
6	2	5	5	2	4	9479.8524	0.0009
6	1	5	6	1	6	6872.2124	-0.0017
6	2	5	6	0	6	6873.2413	-0.0023
6	1	5	5	2	4	9478.8313	-0.0004
6	2	5	5	1	4	9487.3179	-0.0014
7	1	7	6	1	6	9492.6457	-0.0012
7	0	7	6	0	6	9492.6573	0.0015
7	1	6	6	1	5	10748.7447	0.0006
7	2	5	7	2	6	6833.5509	-0.0002
7	3	5	7	1	6	6839.6339	0.0004
8	1	8	7	1	7	10759.1164	0.0006
8	0	8	7	0	7	10759.1164	0.0006
8	1	7	7	1	6	12014.2321	0.0010
8	2	7	7	2	6	12014.1212	0.0016

Table S15. Observed rotational transitions and residuals (in MHz) for $^{13}C_6$ isotopomer of the T1 *o*-anisic acid conformer in the ground vibrational state. See Figure 3 for atom labeling.

J´	**K$_{-1}$´**	**K$_{+1}$´**	**J´´**	**K$_{-1}$´´**	**K$_{+1}$´´**	**Obs.**	**Obs.-Cal.**
3	1	2	2	1	1	5810.6387	-0.0080
3	2	1	2	2	0	6383.2495	-0.0095
4	1	4	3	1	3	5714.7110	-0.0001
4	0	4	3	0	3	5720.9688	-0.0020
4	1	3	3	1	2	7070.1898	0.0015
4	2	2	3	2	1	8295.6458	-0.0006
4	2	3	3	2	2	6896.7565	-0.0003
4	3	1	3	3	0	8469.3600	0.0000
4	3	2	3	3	1	7679.0414	-0.0038
5	1	5	4	1	4	6988.9733	-0.0015
5	0	5	4	0	4	6989.7690	0.0034
5	1	4	4	1	3	8274.8806	-0.0005
5	2	3	4	2	2	9714.9413	0.0008
5	2	4	4	2	3	8234.3244	-0.0009
5	3	3	4	3	2	9304.4242	-0.0013
5	4	2	4	4	1	9848.9808	0.0015
6	1	6	5	1	5	8261.0656	-0.0003
6	0	6	5	0	5	8261.1555	0.0000
6	1	5	5	1	4	9526.7006	-0.0018
6	2	5	5	2	4	9519.9396	-0.0007
6	1	5	6	1	6	6900.4694	-0.0053
6	2	5	6	0	6	6901.5699	0.0007
7	1	7	6	1	6	9532.9150	-0.0017
7	0	7	6	0	6	9532.9253	-0.0009
7	1	6	6	1	5	10794.3598	0.0041
7	2	5	7	2	6	6860.6327	-0.0029
7	3	5	7	1	6	6867.0923	-0.0058
8	1	8	7	1	7	10804.7608	-0.0004
8	0	8	7	0	7	10804.7608	-0.0004
8	1	7	7	1	6	12065.1794	0.0017
8	2	7	7	2	6	12065.0579	0.0000

Table S16. Observed rotational transitions and residuals (in MHz) for $^{13}C_{11}$ isotopomer of the T1 *o*-anisic acid conformer in the ground vibrational state. See Figure 3 for atom labeling.

J´	**K$_{-1}$´**	**K$_{+1}$´**	**J´´**	**K$_{-1}$´´**	**K$_{+1}$´´**	**Obs.**	**Obs.-Cal.**
3	1	2	2	1	1	5803.0881	-0.0015
3	2	1	2	2	0	6323.7851	-0.0016
4	1	4	3	1	3	5713.4760	-0.0032
4	0	4	3	0	3	5721.8201	-0.0007
4	1	3	3	1	2	7083.4826	0.0022
4	2	2	3	2	1	8260.5624	0.0000
4	2	3	3	2	2	6880.9669	0.0009
4	3	1	3	3	0	8363.4851	0.0020
4	3	2	3	3	1	7624.4745	-0.0053
5	1	5	4	1	4	6988.4355	-0.0012
5	0	5	4	0	4	6989.6059	-0.0002
5	1	4	4	1	3	8282.1291	-0.0014
5	2	3	4	2	2	9729.4053	0.0013
5	2	4	4	2	3	8228.8449	-0.0001
5	3	3	4	3	2	9267.0526	-0.0002
5	4	2	4	4	1	9761.7198	-0.0010
6	1	6	5	1	5	8260.5775	-0.0004
6	0	6	5	0	5	8260.7241	-0.0007
6	1	5	5	1	4	9528.4554	0.0009
6	2	5	5	2	4	9518.5442	0.0000
6	1	5	6	1	6	6893.9640	-0.0021
6	2	5	6	0	6	6895.7748	-0.0029
7	1	7	6	1	6	9532.3596	-0.0005
7	0	7	6	0	6	9532.3766	-0.0008
7	1	6	6	1	5	10794.4260	-0.0015
7	3	5	7	1	6	6854.3646	0.0037
8	1	8	7	1	7	10804.1248	0.0026
8	0	8	7	0	7	10804.1248	0.0026
8	1	7	7	1	6	12064.7676	0.0005
8	2	7	7	2	6	12064.5525	0.0015
8	3	5	8	3	6	6756.0949	0.0030
8	4	5	8	2	6	6800.5015	-0.0120
9	4	5	9	4	6	6599.2741	-0.0168

Table S17. Observed rotational transitions and residuals (in MHz) for $^{18}O_{12}$ isotopomer of the T1 *o*-anisic acid conformer in the ground vibrational state. See Figure 3 for atom labeling.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	Obs.	Obs.-Cal.
3	2	1	2	2	0	6381.9252	0.0133
4	1	3	3	1	2	7037.5114	-0.0022
4	2	3	3	2	2	6875.9745	0.0046
4	3	2	3	3	1	7670.8587	-0.0142
5	1	5	4	1	4	6962.1135	-0.0082
5	0	5	4	0	4	6962.7947	0.0050
6	1	6	5	1	5	8229.2790	0.0010
6	0	6	5	0	5	8229.3514	0.0008
6	2	5	6	0	6	6877.0848	0.0177
6	2	5	6	1	6	6877.0848	0.0177
7	1	7	6	1	6	9496.2315	-0.0013
7	0	7	6	0	6	9496.2397	-0.0005
8	1	8	7	1	7	10763.1850	-0.0001
8	0	8	7	0	7	10763.1850	-0.0001
8	4	5	8	2	6	6801.8755	-0.0049
9	3	6	8	5	3	7172.0213	0.0099
9	5	4	8	8	1	7061.1582	0.0022

Table S18. Observed rotational transitions and residuals (in MHz) for $^{2}D_{15}$ isotopomer of the T1 *o*-anisic acid conformer in the ground vibrational state. See Figure 3 for atom labeling.

J′	**$K_{-1}′$**	**$K_{+1}′$**	**J′′**	**$K_{-1}′′$**	**$K_{+1}′′$**	**Obs.**	**Obs.-Cal.**
2	0	2	1	0	1	3230.3556	-0.0080
2	2	0	1	0	1	5879.6983	0.0146
2	2	1	2	0	2	2275.3630	0.0087
2	1	2	1	0	1	3280.8098	-0.0059
2	2	0	1	1	1	5670.6393	0.0158
2	2	1	1	1	0	4764.0910	0.0073
3	1	3	2	1	2	4417.3858	0.0015
3	0	3	2	0	2	4459.9575	0.0025
3	1	2	2	1	1	5798.1799	0.0005
3	1	2	3	1	3	2978.5221	0.0052
3	2	2	3	0	3	3221.8902	-0.0014
3	1	3	2	0	2	4467.8464	0.0100
3	2	2	2	1	1	6033.6725	-0.0002
3	3	1	2	2	0	7599.5077	-0.0010
4	1	4	3	1	3	5704.1499	0.0028
4	0	4	3	0	3	5711.0160	0.0030
4	1	3	3	1	2	7061.8459	0.0020
4	2	3	3	2	2	6879.5696	-0.0012
4	1	3	4	1	4	4336.2058	-0.0079
4	2	2	4	2	3	2711.1699	0.0119
4	2	3	4	0	4	4390.4517	0.0021
4	0	4	3	1	3	5703.1349	0.0033
4	1	4	3	0	3	5712.0311	0.0025
4	1	3	3	2	2	6826.3492	-0.0013
4	2	2	3	3	1	7023.7383	-0.0082
4	2	3	3	1	2	7115.0641	0.0000
4	1	3	4	0	4	4337.2251	-0.0041
5	1	5	4	1	4	6976.3497	0.0060
5	0	5	4	0	4	6977.2458	0.0047
5	3	2	5	3	3	2319.2882	-0.0001
5	4	2	5	2	3	3752.0186	0.0075
5	5	0	5	3	3	7195.3063	0.0050
5	5	1	5	3	2	4828.8852	0.0103
5	0	5	4	1	4	6976.2136	-0.0119
6	2	4	5	4	1	6454.8857	-0.0037
6	3	3	5	5	0	7430.6329	-0.0118
6	2	4	6	2	5	5556.0646	0.0055

Table S18 (Continued).

J′	**K_{-1}′**	**K_{+1}′**	**J′′**	**K_{-1}′′**	**K_{+1}′′**	**Obs.**	**Obs.-Cal.**
6	3	3	6	3	4	3918.1609	-0.0003
6	3	4	6	1	5	5600.1523	0.0106
6	4	3	6	2	4	4482.1845	0.0082
6	6	1	6	4	2	6292.6453	0.0041
6	3	3	6	2	4	3960.9628	-0.0056
6	3	4	6	2	5	5598.8615	-0.0045
7	2	5	7	2	6	6843.3350	0.0153
7	3	4	7	3	5	5421.0481	-0.0015
7	3	5	7	1	6	6850.9284	0.0117
7	4	3	7	4	4	3479.8845	0.0018
7	4	4	7	2	5	5574.6401	-0.0021
7	5	3	7	3	4	4704.2026	0.0039
7	6	2	7	4	3	5419.6905	0.0067
7	2	5	7	1	6	6843.4818	-0.0028
7	4	4	7	3	5	5567.2032	-0.0070
8	3	5	8	3	6	6770.1358	-0.0005
8	4	4	8	4	5	5165.1959	-0.0042
8	4	5	8	2	6	6802.0386	-0.0003
8	5	3	8	5	4	2907.7347	0.0085
8	5	4	8	3	5	5586.6405	-0.0050
8	6	3	8	4	4	5168.3340	-0.0037
8	7	2	8	5	3	6774.6325	-0.0054
8	3	5	8	2	6	6771.2548	-0.0094
8	4	4	8	3	5	5195.9685	-0.0063
8	4	5	8	3	6	6800.9117	0.0006
8	5	4	8	4	5	5555.8699	-0.0010
8	6	3	8	5	4	4777.6702	0.0032
9	4	5	9	4	6	6642.1510	-0.0020
9	5	4	9	5	5	4739.5534	0.0023
9	5	5	9	3	6	6748.1845	-0.0018
9	6	4	9	4	5	5694.0320	-0.0035
9	7	3	9	5	4	5969.8237	-0.0137
10	4	6	10	4	7	7978.6640	-0.0056
10	5	5	10	5	6	6416.9429	-0.0009
10	6	4	10	6	5	4135.4771	-0.0023
10	6	5	10	4	6	6710.1805	-0.0067
10	7	4	10	5	5	5984.0892	-0.0061
10	8	3	10	6	4	7152.5203	0.0044

Table S18 (Continued).

J´	K$_{-1}$´	K$_{+1}$´	J´´	K$_{-1}$´´	K$_{+1}$´´	Obs.	Obs.-Cal.
10	4	6	10	3	7	7979.5319	0.0012
11	5	6	11	5	7	7855.8678	-0.0073
11	6	5	11	6	6	6038.1807	-0.0030
11	6	6	11	4	7	7925.7572	0.0043
11	7	4	11	7	5	3396.3453	0.0098
11	7	5	11	5	6	6729.8976	0.0007
12	10	2	12	9	3	6265.6997	-0.0032
13	9	5	13	7	6	7249.1763	-0.0138

Table S19. Observed rotational transitions and residuals (in MHz) for $^{13}C_{16}$ isotopomer of the T1 *o*-anisic acid conformer in the ground vibrational state. See Figure 3 for atom labeling.

J′	**K_{-1}′**	**K_{+1}′**	**J′′**	**K_{-1}′′**	**K_{+1}′′**	**Obs.**	**Obs.-Cal.**
2	2	0	1	0	1	5829.4269	0.0110
3	2	1	2	2	0	6350.6088	0.0005
4	1	4	3	1	3	5671.9981	-0.0014
4	0	4	3	0	3	5677.7408	0.0000
4	1	3	3	1	2	7013.6036	-0.0001
4	2	2	3	2	1	8241.6330	-0.0013
4	2	3	3	2	2	6848.8090	-0.0003
4	3	1	3	3	0	8433.0848	0.0000
4	3	2	3	3	1	7635.4475	0.0005
5	1	5	4	1	4	6936.5071	-0.0011
5	0	5	4	0	4	6937.2120	-0.0012
5	1	4	4	1	3	8211.0200	-0.0005
5	2	3	4	2	2	9637.4689	0.0029
5	2	4	4	2	3	8173.6931	-0.0029
5	3	3	4	3	2	9243.7949	0.0006
6	1	6	5	1	5	8199.0098	-0.0009
6	0	6	5	0	5	8199.0899	0.0014
6	1	5	5	1	4	9454.7206	0.0013
6	2	4	5	2	3	10787.5241	-0.0039
6	2	5	5	2	4	9448.6781	0.0004
7	1	7	6	1	6	9461.2958	-0.0042
7	0	7	6	0	6	9461.3086	0.0005
7	1	6	6	1	5	10713.1953	-0.0005
7	2	5	7	2	6	6813.3903	-0.0036
7	3	5	7	1	6	6818.9874	-0.0003
8	1	8	7	1	7	10723.5859	0.0003
8	0	8	7	0	7	10723.5859	0.0003
8	1	7	7	1	6	11974.5520	0.0004
8	2	7	7	2	6	11974.4547	0.0041
8	3	5	8	3	6	6751.0746	0.0082
8	4	5	8	2	6	6774.6720	0.0065
9	1	9	8	1	8	11985.8825	0.0028
9	0	9	8	0	8	11985.8825	0.0028

Table S20. Observed rotational transitions and residuals (in MHz) for the C2 conformer of *o*-anisic acid in the ground vibrational state (0^+).

J'	**K_{-1}'**	**K_{+1}'**	**J''**	**K_{-1}''**	**K_{+1}''**	**Obs.**	**Obs.-Cal.**
2	1	2	1	1	1	3078.6587	-0.0005
2	1	1	1	1	0	4108.8244	-0.0037
2	2	0	1	0	1	5929.4683	-0.0088
3	1	3	2	1	2	4443.7300	0.0007
3	0	3	2	0	2	4498.4733	0.0031
3	1	2	2	1	1	5807.9128	-0.0009
3	2	1	2	2	0	6282.7553	0.0003
3	2	2	2	2	1	5390.6133	0.0009
3	2	2	2	1	1	6114.2106	-0.0016
3	3	0	2	2	1	8239.6486	0.0007
3	3	1	2	2	0	7717.8148	-0.0010
4	0	4	3	0	3	5757.4504	-0.0024
4	1	3	3	1	2	7117.1646	0.0000
4	2	2	3	2	1	8241.0031	0.0003
4	2	3	3	2	2	6891.7784	-0.0024
4	3	1	3	3	0	8287.9606	0.0032
4	3	2	3	3	1	7597.6650	0.0049
4	0	4	3	1	3	5745.3051	-0.0086
4	1	4	3	0	3	5759.2698	0.0025
4	1	3	3	2	2	6810.8517	-0.0144
4	2	2	3	3	1	6805.9386	-0.0033
4	2	3	3	1	2	7198.0793	-0.0001
4	3	2	3	2	1	9032.7217	0.0008
5	1	5	4	1	4	7032.7813	-0.0026
5	0	5	4	0	4	7034.3513	-0.0024
5	1	4	4	1	3	8322.8479	-0.0012
5	2	3	4	2	2	9758.5440	0.0002
5	2	4	4	2	3	8257.7567	0.0006
5	3	2	4	3	1	10512.7964	0.0013
5	3	3	4	3	2	9259.6331	0.0008
5	4	2	4	4	1	9710.9193	0.0005
5	2	3	5	2	4	4082.9214	0.0047
5	2	4	5	0	5	5585.6099	0.0038
5	0	5	4	1	4	7032.5293	-0.0099
5	1	5	4	0	4	7034.6036	0.0051
5	1	4	4	2	3	8241.9338	-0.0006

Table S20 (Continued).

J´	K-1´	K+1´	J´´	K-1´´	K+1´´	Obs.	Obs.-Cal.
5	2	3	4	3	2	8966.8252	-0.0004
5	2	4	4	1	3	8338.6712	0.0004
6	1	6	5	1	5	8315.0367	0.0001
6	0	6	5	0	5	8315.2522	0.0019
6	1	5	5	1	4	9574.4070	0.0008
6	2	4	5	2	3	10951.4597	-0.0006
6	2	5	5	2	4	9561.2105	0.0000
6	3	4	5	3	3	10733.3279	-0.0005
6	2	4	6	2	5	5473.1633	-0.0032
6	2	5	6	0	6	6831.5710	0.0047
6	0	6	5	1	5	8315.0092	0.0036
6	1	6	5	0	5	8315.2815	0.0003
6	1	5	5	2	4	9558.5841	-0.0003
6	2	4	5	3	3	10658.6531	-0.0007
6	2	5	5	1	4	9577.0304	-0.0018
6	3	4	5	4	1	6549.5908	0.0005
6	4	3	5	5	0	7645.9998	0.0011
7	1	7	6	1	6	9596.8060	0.0014
7	0	7	6	0	6	9596.8315	-0.0002
7	1	6	6	1	5	10848.7594	-0.0003
7	2	6	6	2	5	10846.5276	0.0000
7	3	5	6	3	4	12082.7133	-0.0024
7	1	6	7	1	7	8080.8793	0.0149
7	2	5	7	2	6	6768.8859	-0.0051
7	3	4	7	3	5	5271.8841	0.0069
7	3	5	7	1	6	6784.4175	-0.0058
7	6	2	7	4	3	6093.9205	-0.0100
7	3	5	6	4	2	6035.4157	-0.0004
7	2	5	7	1	6	6769.2779	-0.0071
8	1	8	7	1	7	10878.5302	-0.0003
8	0	8	7	0	7	10878.5342	0.0003
8	3	5	8	3	6	6661.3384	-0.0033
8	4	5	8	2	6	6725.6243	-0.0032
8	7	2	8	5	3	7741.0255	0.0046
8	3	5	8	2	6	6664.0091	-0.0048
8	4	5	8	3	6	6722.9513	-0.0041
8	8	0	8	7	1	6177.9741	0.0105

Table S20 (Continued).

J′	**K$_{-1}$′**	**K$_{+1}$′**	**J′′**	**K$_{-1}$′′**	**K$_{+1}$′′**	**Obs.**	**Obs.-Cal.**
8	8	1	8	7	2	6229.7283	0.0009
9	3	6	9	3	7	7959.5553	-0.0031
9	4	5	9	4	6	6464.0121	-0.0024
9	4	6	9	2	7	7972.7426	-0.0044
9	5	5	9	3	6	6672.5900	0.0006
9	7	3	9	5	4	6701.8934	-0.0002
9	3	6	9	2	7	7959.9863	-0.0017
9	4	5	9	3	6	6476.7780	0.0045
9	4	6	9	3	7	7972.3178	0.0003
9	5	5	9	4	6	6659.8317	0.0013
9	8	2	9	7	3	6052.6578	-0.0082
9	9	0	9	8	1	7057.6270	-0.0064
10	4	6	10	4	7	7843.8230	-0.0007
10	5	5	10	5	6	6111.5443	-0.0009
10	5	6	10	3	7	7893.9419	-0.0070
10	6	5	10	4	6	6666.7749	0.0085
10	7	4	10	5	5	6339.6168	-0.0075
10	5	5	10	4	6	6159.3322	0.0074
10	6	5	10	5	6	6618.9861	-0.0008
11	5	6	11	5	7	7652.7525	-0.0010
11	6	6	11	4	7	7810.6937	-0.0026
11	8	4	11	6	5	7275.5560	0.0076
11	7	5	11	6	6	6636.1870	-0.0010
11	8	4	11	7	5	6181.4635	-0.0008
11	9	2	11	8	3	6092.3831	-0.0029
11	9	3	11	8	4	6683.1190	0.0004
11	10	1	11	9	2	7645.6698	0.0133
12	6	6	12	6	7	7329.4481	0.0083
12	7	6	12	5	7	7753.1505	-0.0042
12	8	5	12	7	6	6751.3194	0.0093
13	7	6	13	6	7	6909.9496	0.0047
13	9	5	13	8	6	6997.8451	-0.0090

Table S21. Observed rotational transitions and residuals (in MHz) for $^{2}D_{15}$ isotopologue of the C2 *o*-anisic acid conformer in the ground vibrational state (0^{+}). See Figure 3 for atom labeling.

J´	**K_{-1}´**	**K_{+1}´**	**J´´**	**K_{-1}´´**	**K_{+1}´´**	**Obs.**	**Obs.-Cal.**
2	1	1	1	1	0	4025.7488	-0.0124
3	1	3	2	1	2	4376.7964	-0.0030
3	0	3	2	0	2	4439.4350	-0.0044
3	1	2	2	1	1	5716.1642	0.0070
3	2	1	2	2	0	6139.0453	0.0005
3	1	3	2	0	2	4454.9371	0.0086
3	3	1	2	2	0	7683.8287	-0.0045
4	1	4	3	1	3	5664.6909	0.0080
4	1	3	3	1	2	7029.9308	-0.0059
4	0	4	3	1	3	5662.1561	-0.0003
4	1	4	3	0	3	5680.1743	0.0024
4	1	3	3	2	2	6676.7082	-0.0051
5	1	5	4	1	4	6932.9846	0.0082
5	0	5	4	0	4	6935.1383	0.0071
5	2	4	4	2	3	8135.7121	-0.0046
5	0	5	4	1	4	6932.6107	0.0059
5	1	5	4	0	4	6935.5100	0.0072
6	1	6	5	1	5	8197.1169	-0.0093
6	0	6	5	0	5	8197.4387	-0.0079
7	2	5	7	2	6	6659.8930	0.0053

Table S22. Observed rotational transitions and residuals (in MHz) for the C1 conformer of *o*-anisic acid in the ground vibrational state.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	Obs.	Obs.-Cal.
2	1	1	1	1	0	4075.8266	0.0113
3	1	3	2	1	2	4427.4172	-0.0003
3	0	3	2	0	2	4489.0453	-0.0112
3	1	2	2	1	1	5782.6022	-0.0018
3	2	1	2	2	0	6218.5445	-0.0008
3	2	2	2	2	1	5353.8042	0.0032
3	2	2	2	1	1	6129.6671	-0.0009
3	3	1	2	2	0	7755.3493	0.0078
4	1	4	3	1	3	5729.4716	-0.0044
4	0	4	3	0	3	5742.0153	-0.0015
4	1	3	3	1	2	7106.9404	-0.0001
4	2	2	3	2	1	8185.2685	-0.0007
4	2	3	3	2	2	6858.6784	-0.0027
4	3	2	3	3	1	7534.0899	-0.0027
4	1	3	3	3	0	3869.1254	0.0084
4	1	3	3	2	2	6759.8662	-0.0102
4	2	3	3	1	2	7205.7535	0.0082
5	1	5	4	1	4	7012.1263	-0.0007
5	0	5	4	0	4	7014.1757	-0.0022
5	1	4	4	1	3	8307.0074	0.0005
5	2	3	4	2	2	9735.4021	0.0021
5	2	4	4	2	3	8229.0091	0.0002
5	3	3	4	3	2	9201.8834	-0.0022
5	0	5	4	1	4	7011.7820	0.0021
5	1	5	4	0	4	7014.5195	-0.0057
5	2	3	4	3	2	8849.7824	0.0019
6	1	6	5	1	5	8290.7460	0.0000
6	0	6	5	0	5	8291.0460	0.0000
6	1	5	5	1	4	9549.8207	-0.0004
6	2	4	5	2	3	10941.7661	0.0026
6	2	5	5	2	4	9532.7261	-0.0005
6	1	5	6	1	6	6806.4429	-0.0017
6	2	5	6	0	6	6810.1952	-0.0088
7	1	6	6	1	5	10818.5434	-0.0016
7	2	6	6	2	5	10815.4292	-0.0019
7	2	5	7	2	6	6735.4158	-0.0012
7	3	5	7	1	6	6757.2716	-0.0054

Table S22 (Continued).

J´	**K$_{-1}$´**	**K$_{+1}$´**	**J´´**	**K$_{-1}$´´**	**K$_{+1}$´´**	**Obs.**	**Obs.-Cal.**
7	2	5	7	1	6	6736.0250	0.0097
7	3	5	7	2	6	6756.6765	-0.0022
8	1	8	7	1	7	10846.6623	0.0002
8	0	8	7	0	7	10846.6695	0.0020
8	2	6	8	2	7	8000.5440	0.0086
8	3	5	8	3	6	6604.7594	-0.0040
8	3	6	8	1	7	8004.6628	0.0001
8	4	5	8	2	6	6694.4106	-0.0049
9	1	9	8	1	8	12124.5924	-0.0005
9	0	9	8	0	8	12124.5924	-0.0005
9	4	5	9	4	6	6360.3575	0.0002

Table S23. Observed rotational transitions and residuals (in MHz) for the C2 conformer of *o*-anisic acid in the first vibrational state (0^-).

J´	**K_{-1}´**	**K_{+1}´**	**J´´**	**K_{-1}´´**	**K_{+1}´´**	**Obs.**	**Obs.-Cal.**
3	2	1	2	2	0	6276.1529	-0.0045
3	2	2	2	1	1	6117.9130	-0.0016
4	1	3	3	1	2	7123.3436	-0.0049
4	2	3	3	2	2	6896.2776	0.0044
4	3	2	3	3	1	7595.1499	0.0005
4	1	3	3	2	2	6813.7283	0.0104
5	1	5	4	1	4	7048.2504	-0.0027
5	0	5	4	0	4	7049.8660	-0.0023
5	1	4	4	1	3	8332.8189	0.0029
5	2	3	4	2	2	9761.1584	-0.0001
5	0	5	4	1	4	7048.0006	0.0016
5	1	5	4	0	4	7050.1086	-0.0140
6	1	6	5	1	5	8334.2402	-0.0008
6	0	6	5	0	5	8334.4623	-0.0005
6	1	5	5	1	4	9587.6562	0.0007
6	2	5	5	2	4	9574.0919	-0.0009
7	1	7	6	1	6	9619.7325	0.0010
7	0	7	6	0	6	9619.7587	-0.0012
7	1	6	6	1	5	10865.5601	0.0000
7	2	5	7	2	6	6733.3039	-0.0015
7	2	5	7	1	6	6733.7176	-0.0008
8	1	8	7	1	7	10905.1818	0.0014
8	0	8	7	0	7	10905.1818	0.0014
8	1	7	7	1	6	12149.1218	-0.0010
9	4	6	8	5	3	7956.8263	0.0002

Table S24. Observed rotational transitions and residuals (in MHz) for the T1-w-1 conformer of *o*-anisic acid-water complex in the ground vibrational state.

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	**Obs.**	**Obs.-Cal.**
2	1	1	1	1	0	2401.6088	-0.0066
3	1	3	2	1	2	2902.7839	-0.0035
3	0	3	2	0	2	3076.2787	0.0071
3	1	2	2	1	1	3565.3525	-0.0020
3	2	1	2	0	2	6403.9012	-0.0096
3	2	1	2	2	0	3458.2661	0.0056
3	2	2	2	2	1	3267.2680	0.0012
3	2	1	2	1	2	5976.7832	0.0078
3	2	2	2	1	1	5063.7160	-0.0029
3	3	0	2	2	1	6856.9990	-0.0079
3	3	1	2	2	0	6797.5146	0.0001
4	1	4	3	1	3	3825.1008	-0.0003
4	0	4	3	0	3	3950.1770	-0.0015
4	1	3	3	1	2	4674.1589	-0.0011
4	2	2	3	2	1	4720.7719	-0.0015
4	2	3	3	2	2	4315.5585	-0.0010
4	3	1	3	3	0	4485.4074	0.0002
4	3	2	3	3	1	4440.7290	-0.0011
4	2	3	3	1	2	5813.9194	-0.0045
4	4	0	3	3	1	9342.5171	0.0026
4	4	1	3	3	0	9333.8219	0.0005
5	1	5	4	1	4	4724.8828	-0.0012
5	0	5	4	0	4	4795.1990	-0.0006
5	1	4	4	1	3	5698.3988	-0.0009
5	2	3	4	2	2	5973.7251	-0.0026
5	2	4	4	2	3	5330.9591	-0.0007
5	3	2	4	3	1	5701.2560	-0.0013
5	3	3	4	3	2	5557.7159	-0.0012
5	4	1	4	4	0	5567.3530	-0.0024
5	4	2	4	4	1	5559.9007	0.0010
5	1	4	5	1	5	3155.4464	-0.0039
5	2	4	5	0	5	3986.0350	0.0021
5	2	4	4	1	3	6470.7198	-0.0039
5	3	2	4	2	3	9460.8495	0.0043
5	3	3	4	2	2	8616.9271	-0.0007
6	1	6	5	1	5	5608.6684	-0.0011
6	0	6	5	0	5	5642.3879	-0.0012

Table S24 (Continued).

J´	K-1´	K+1´	J´´	K-1´´	K+1´´	Obs.	Obs.-Cal.
6	1	5	5	1	4	6622.2772	-0.0003
6	2	4	5	2	3	7169.9131	-0.0028
6	2	5	5	2	4	6309.8836	-0.0013
6	3	3	5	3	2	6983.7396	-0.0021
6	3	4	5	3	3	6657.8084	-0.0015
6	4	2	5	4	1	6732.8446	-0.0041
6	4	3	5	4	2	6700.7866	-0.0010
6	5	1	5	5	0	6667.7718	-0.0053
6	2	5	6	0	6	4653.5229	-0.0056
6	3	4	6	1	5	4741.7852	-0.0008
6	0	6	5	1	5	5584.1361	0.0054
6	1	6	5	0	5	5666.9262	-0.0018
6	1	5	5	2	4	5849.9537	0.0001
6	3	4	5	2	3	9301.0068	-0.0033
6	5	2	6	4	3	6255.1718	0.0030
7	1	7	6	1	6	6482.9256	-0.0016
7	0	7	6	0	6	6497.6207	-0.0008
7	1	6	6	1	5	7470.3523	0.0000
7	2	5	6	2	4	8280.6060	0.0005
7	2	6	6	2	5	7253.4245	-0.0003
7	3	4	6	3	3	8299.8231	0.0014
7	3	5	6	3	4	7728.8146	-0.0022
7	4	3	6	4	2	7943.8087	-0.0006
7	4	4	6	4	3	7845.1876	-0.0020
7	5	2	6	5	1	7815.4939	-0.0043
7	5	3	6	5	2	7809.9304	-0.0003
7	1	6	7	1	7	5156.4798	-0.0036
7	2	5	7	2	6	3177.9407	-0.0005
7	2	6	7	0	7	5409.3279	-0.0039
7	3	5	7	1	6	5000.2438	-0.0067
7	4	4	7	2	5	6641.6698	0.0015
7	0	7	6	1	6	6473.0813	-0.0013
7	1	7	6	0	6	6507.4754	0.0092
7	3	5	6	2	4	9859.9106	-0.0003
7	2	6	7	1	7	5399.4783	-0.0089
7	4	3	7	3	4	4108.5701	0.0084
7	4	4	7	3	5	5062.3520	-0.0107
8	1	8	7	1	7	7352.2642	-0.0007

Table S24 (Continued).

J´	K_{-1}´	K_{+1}´	J´´	K_{-1}´´	K_{+1}´´	Obs.	Obs.-Cal.
8	0	8	7	0	7	7358.2930	-0.0009
8	1	7	7	1	6	8293.2540	0.0001
8	2	6	7	2	5	9284.0064	-0.0008
8	2	7	7	2	6	8167.2305	-0.0006
8	3	5	7	3	4	9587.3140	-0.0019
8	3	6	7	3	5	8762.1246	0.0009
8	4	4	7	4	3	9218.8303	-0.0015
8	4	5	7	4	4	8982.1313	0.0000
8	5	3	7	5	2	8985.9455	0.0006
8	5	4	7	5	3	8964.7352	0.0005
8	6	2	7	6	1	8913.5958	-0.0014
8	6	3	7	6	2	8912.7646	0.0005
8	1	7	8	1	8	6097.4696	-0.0027
8	2	6	8	2	7	4294.7133	-0.0041
8	2	7	8	0	8	6218.2645	-0.0045
8	3	6	8	1	7	5469.1151	-0.0051
8	4	5	8	2	6	6339.7920	-0.0002
8	5	4	8	3	5	9566.7984	-0.0006
8	0	8	7	1	7	7348.4473	-0.0019
8	1	8	7	0	7	7362.1046	-0.0050
8	2	7	7	1	6	8410.2369	0.0020
8	2	7	8	1	8	6214.4413	-0.0120
9	1	9	8	1	8	8219.3326	-0.0005
9	0	9	8	0	8	8221.7072	-0.0003
9	1	8	8	1	7	9123.7820	0.0005
9	2	7	8	2	6	10177.6648	0.0008
9	2	7	8	4	4	3462.0690	-0.0109
9	2	8	8	2	7	9059.4882	-0.0005
9	3	6	8	3	5	10796.4832	0.0000
9	3	7	8	3	6	9754.1676	0.0001
9	7	2	8	7	1	10015.8744	-0.0012
9	8	1	8	8	0	9983.5517	0.0022
9	8	2	8	8	1	9983.5517	0.0022
9	1	8	9	1	9	7001.9210	0.0004
9	2	7	9	2	8	5412.8938	0.0010
9	2	8	9	0	9	7056.0408	-0.0094
9	3	7	9	1	8	6099.5056	-0.0007
9	4	6	9	2	7	6260.5068	0.0032

Table S24 (Continued).

J′	**K_{-1}'**	**K_{+1}'**	**J′′**	**K_{-1}''**	**K_{+1}''**	**Obs.**	**Obs.-Cal.**
9	0	9	8	1	8	8217.8920	0.0001
9	1	9	8	0	8	8223.1466	-0.0022
9	1	8	8	2	7	9006.8011	0.0006
9	2	7	8	3	6	9120.2413	-0.0009
9	2	8	8	1	7	9176.4701	0.0003
9	3	7	9	2	8	6046.8154	-0.0026
9	4	6	9	3	7	5626.5640	-0.0142
9	5	5	9	4	6	6231.6333	-0.0150
9	6	3	9	5	4	7453.1635	0.0028
10	1	10	9	1	9	9085.4449	-0.0007
10	0	10	9	0	9	9086.3527	-0.0005
10	1	9	9	1	8	9968.2750	0.0008
10	2	9	9	2	8	9938.2064	-0.0008
10	2	8	10	2	9	6472.3457	-0.0090
10	2	9	10	0	10	7907.9049	0.0007
10	3	8	10	1	9	6838.0599	-0.0060
10	4	7	10	2	8	6444.5619	0.0003
10	0	10	9	1	9	9084.9114	-0.0004
10	1	10	9	0	9	9086.8881	0.0011
10	1	9	9	2	8	9915.5858	0.0000
10	2	9	9	1	8	9990.8974	0.0018
11	1	11	10	1	10	9951.1864	-0.0008
11	0	11	10	0	10	9951.5277	0.0012
11	1	10	11	1	11	8756.2725	-0.0003
11	2	9	11	2	10	7461.4295	0.0122
11	0	11	10	1	10	9950.9929	0.0001
11	1	11	10	0	10	9951.7208	-0.0001
12	1	11	12	1	12	9622.1216	-0.0001
12	2	10	12	2	11	8397.3473	-0.0003
12	2	11	12	0	12	9625.9659	0.0007
12	3	10	12	1	11	8481.4602	-0.0006
13	3	11	13	1	12	9338.4408	0.0007
13	4	10	13	2	11	8209.6701	-0.0017
14	3	11	14	3	12	8779.6097	0.0016
14	4	11	14	2	12	9014.8143	0.0039
15	4	12	15	2	13	9860.4032	-0.0033

Table S25. Observed rotational transitions and residuals (in MHz) for $^{2}D_{15}$ isotopomer of the T1-w-1 *o*-anisic acid-water complex in the ground vibrational state. See Figure 3 for atom labeling.

J´	**K$_{-1}$´**	**K$_{+1}$´**	**J´´**	**K$_{-1}$´´**	**K$_{+1}$´´**	**Obs.**	**Obs.-Cal.**
2	2	0	1	1	1	4429.3138	0.0162
3	0	3	2	0	2	3063.0281	-0.0097
3	1	2	2	1	1	3558.4376	0.0158
4	1	4	3	1	3	3809.4276	0.0004
4	0	4	3	0	3	3930.6403	0.0007
4	1	3	3	1	2	4661.8191	-0.0002
4	3	1	3	3	0	4479.8900	-0.0114
4	3	2	3	3	1	4432.6411	0.0106
5	1	5	4	1	4	4704.2564	-0.0007
5	0	5	4	0	4	4771.0799	0.0060
5	2	3	4	2	2	5967.5124	-0.0085
5	2	4	4	2	3	5314.2818	-0.0041
5	2	4	4	1	3	6410.3724	-0.0027
6	1	6	5	1	5	5583.2076	-0.0009
6	0	6	5	0	5	5614.6493	-0.0006
6	1	5	5	1	4	6591.2574	-0.0034
6	2	4	5	2	3	7156.8824	-0.0016
6	2	5	5	2	4	6287.4386	0.0026
6	3	3	5	3	2	6983.4485	-0.0060
6	3	4	5	3	3	6643.1869	-0.0113
6	1	5	5	2	4	5858.4839	0.0186
7	1	7	6	1	6	6452.8800	0.0048
7	0	7	6	0	6	6466.3289	-0.0042
7	1	6	6	1	5	7431.2474	-0.0004
7	2	6	6	2	5	7224.7448	0.0000
7	3	5	6	3	4	7708.9158	0.0000
7	4	3	6	4	2	7938.8892	-0.0048
7	4	4	6	4	3	7832.4565	-0.0038
8	1	8	7	1	7	7317.8448	0.0042
8	0	8	7	0	7	7323.2721	0.0045
8	3	6	8	1	7	5424.0504	-0.0152
8	2	6	7	3	5	7750.2258	0.0005
10	2	9	10	1	10	7878.4492	0.0105

Table S26. Observed rotational transitions and residuals (in MHz) for ${}^2D_{20}$ isotopomer of the T1-w-1 *o*-anisic acid-water complex in the ground vibrational state. See Figure 3 for atom labeling.

J′	K_{-1}′	K_{+1}′	J′′	K_{-1}′′	K_{+1}′′	Obs.	Obs.-Cal.
3	1	3	2	1	2	2867.2579	-0.0060
3	0	3	2	0	2	3040.8615	0.0064
3	1	2	2	1	1	3512.6178	0.0034
3	2	1	2	2	0	3401.2152	-0.0060
3	2	2	2	2	1	3221.0344	-0.0045
4	1	4	3	1	3	3780.0872	0.0001
4	0	4	3	0	3	3908.4125	0.0035
4	1	3	3	1	2	4609.4074	0.0067
4	2	2	3	2	1	4641.9373	0.0025
4	2	3	3	2	2	4256.4620	-0.0018
4	3	1	3	3	0	4414.9148	0.0001
4	3	2	3	3	1	4374.4357	-0.0117
5	1	5	4	1	4	4671.0633	-0.0021
5	0	5	4	0	4	4745.2328	0.0006
5	1	4	4	1	3	5627.3216	0.0025
5	2	3	4	2	2	5877.5634	0.0017
5	2	4	4	2	3	5260.9116	0.0014
5	3	2	4	3	1	5606.4132	-0.0050
5	3	3	4	3	2	5475.5427	0.0001
5	4	1	4	4	0	5482.3493	-0.0001
5	4	2	4	4	1	5475.8471	-0.0092
5	5	0	5	4	1	6354.8495	0.0035
6	1	6	5	1	5	5546.1858	-0.0010
6	0	6	5	0	5	5582.7211	0.0019
6	1	5	5	1	4	6549.3275	0.0131
6	2	4	5	2	3	7062.0096	0.0042
6	2	5	5	2	4	6230.7202	0.0030
6	3	3	5	3	2	6862.2925	-0.0025
6	3	4	5	3	3	6561.6507	0.0043
6	4	2	5	4	1	6626.7384	-0.0036
6	4	3	5	4	2	6598.7240	0.0022
6	5	1	5	5	0	6566.8498	-0.0033
7	1	7	6	1	6	6411.6129	-0.0056
7	0	7	6	0	6	6427.9464	-0.0015
7	1	6	6	1	5	7394.3987	0.0163
7	2	6	6	2	5	7166.4514	0.0057
7	3	5	6	3	4	7621.1398	0.0055

Table S26 (Continued).

J´	**K_{-1}'**	**K_{+1}'**	**J´´**	**K_{-1}''**	**K_{+1}''**	**Obs.**	**Obs.-Cal.**
7	4	3	6	4	2	7812.5583	-0.0060
7	4	4	6	4	3	7725.8059	0.0027
7	5	2	6	5	1	7695.1858	-0.0044
7	5	3	6	5	2	7690.5085	-0.0053
7	4	4	7	2	5	6770.7805	-0.0012
8	1	8	7	1	7	7271.9009	-0.0053
8	0	8	7	0	7	7278.7664	-0.0056
9	5	4	9	4	5	5622.9606	-0.0059

Table S27. Observed rotational transitions and residuals (in MHz) for $^{18}O_{21}$ isotopomer of the T1-w-1 *o*-anisic acid-water complex in the ground vibrational state. See Figure 3 for atom labeling.

J´	**K_{-1}´**	**K_{+1}´**	**J´´**	**K_{-1}´´**	**K_{+1}´´**	**Obs.**	**Obs.-Cal.**
7	1	7	6	1	6	6283.3876	0.0003
7	0	7	6	0	6	6302.8977	0.0013
7	1	6	6	1	5	7256.2682	-0.0001
7	2	5	6	2	4	7962.7376	0.0006
7	2	6	6	2	5	7010.0393	0.0001
7	0	7	6	1	6	6268.8090	-0.0015
7	1	7	6	0	6	6317.4745	0.0014
8	1	8	7	1	7	7127.4436	0.0000
8	0	8	7	0	7	7136.0011	0.0001
8	1	7	7	1	6	8059.0690	-0.0010
8	2	6	7	2	5	8967.2147	-0.0005
8	2	7	7	2	6	7903.1443	-0.0002
8	0	8	7	1	7	7121.4197	-0.0045
8	1	8	7	0	7	7142.0217	0.0014
9	1	9	8	1	8	7968.7487	-0.0017
9	0	9	8	0	8	7972.3479	-0.0001
9	1	8	8	1	7	8860.7494	0.0001
9	2	7	8	2	6	9872.2067	0.0000
9	2	8	8	2	7	8774.4322	0.0011
9	0	9	8	1	8	7966.3314	0.0026
9	1	9	8	0	8	7974.7704	0.0005

Table S28. Observed rotational transitions and residuals (in MHz) for $^2D_{15}$-$^2D_{20}$ isotopomers of the T1-w-1 *o*-anisic acid-water complex in the ground vibrational state. See Figure 3 for atom labeling.

J′	**K_{-1}′**	**K_{+1}′**	**J′′**	**K_{-1}′′**	**K_{+1}′′**	**Obs.**	**Obs.-Cal.**
3	0	3	2	0	2	3027.9903	-0.0163
3	1	2	2	1	1	3505.8284	-0.0017
4	1	4	3	1	3	3764.7409	0.0054
4	0	4	3	0	3	3889.3147	-0.0047
4	1	3	3	1	2	4597.4999	0.0004
4	2	2	3	2	1	4639.1435	-0.0028
5	1	5	4	1	4	4650.8647	0.0003
5	0	5	4	0	4	4721.5064	-0.0049
5	2	3	4	2	2	5871.6091	0.0086
5	2	4	4	2	3	5244.6334	-0.0024
5	3	2	4	3	1	5602.7049	-0.0035
5	3	3	4	3	2	5464.8726	-0.0145
5	4	1	4	4	0	5473.5060	0.0055
5	4	2	4	4	1	5466.4469	0.0035
5	2	4	5	1	5	3871.7778	-0.0106
6	1	6	5	1	5	5521.2291	0.0011
6	0	6	5	0	5	5555.3890	-0.0016
6	2	4	5	2	3	7049.7124	0.0000
6	2	5	5	2	4	6208.8700	-0.0003
6	3	4	5	3	3	6547.3276	-0.0015
6	4	2	5	4	1	6618.2886	-0.0125
6	4	3	5	4	2	6587.9064	-0.0136
6	1	5	6	1	6	4093.5025	-0.0165
6	6	1	6	5	2	7626.8961	0.0059
6	2	5	5	1	4	6985.3977	-0.0025
7	1	7	6	1	6	6382.1269	0.0007
7	0	7	6	0	6	6397.1324	0.0005
7	2	6	6	2	5	7138.5389	-0.0054
7	3	5	6	3	4	7601.8109	0.0028
7	4	4	6	4	3	7713.1120	0.0134
7	5	2	6	5	1	7683.4479	0.0099
7	5	3	6	5	2	7678.2205	-0.0062
8	1	8	7	1	7	7238.1004	0.0062
8	0	8	7	0	7	7244.3040	0.0059
8	2	7	7	2	6	8038.9795	-0.0124
8	0	8	7	1	7	7234.1236	0.0028
8	1	8	7	0	7	7248.2746	0.0031

Table S28 (Continued).

J´	K_{-1}´	K_{+1}´	J´´	K_{-1}´´	K_{+1}´´	Obs.	Obs.-Cal.
8	2	6	8	1	7	4322.8495	0.0129
9	1	9	8	1	8	8091.7717	0.0044
9	0	9	8	0	8	8094.2390	0.0100
10	3	7	10	2	8	4396.8731	0.0094

Table S29. Observed rotational transitions and residuals (in MHz) for $^2D_{20}$-$^2D_{22}$ isotopomers of the T1-w-1 *o*-anisic acid-water complex in the ground vibrational state. See Figure 3 for atom labeling.

J´	**K$_{-1}$´**	**K$_{+1}$´**	**J´´**	**K$_{-1}$´´**	**K$_{+1}$´´**	**Obs.**	**Obs.-Cal.**
3	0	3	2	0	2	2973.1788	-0.0017
3	1	2	2	1	1	3413.1533	-0.0006
3	2	1	2	2	0	3294.8880	0.0102
3	2	2	2	2	1	3134.0401	0.0101
3	2	2	2	1	1	5020.4467	0.0160
4	1	4	3	1	3	3694.7140	-0.0041
4	0	4	3	0	3	3828.6743	0.0007
4	1	3	3	1	2	4486.4042	-0.0121
4	3	2	4	1	3	5055.2375	-0.0036
5	1	5	4	1	4	4568.8964	0.0124
5	0	5	4	0	4	4650.3987	-0.0032
5	1	4	4	1	3	5490.9001	0.0004
5	2	3	4	2	2	5696.2082	-0.0154
5	2	4	4	2	3	5128.2351	-0.0031
5	3	2	4	3	1	5430.3952	-0.0097
5	3	3	4	3	2	5321.0864	-0.0077
6	1	6	5	1	5	5427.5629	0.0029
6	0	6	5	0	5	5469.7869	0.0036
6	1	5	5	1	4	6408.3179	-0.0008
6	2	4	5	2	3	6856.9126	-0.0050
6	2	5	5	2	4	6080.2829	-0.0006
6	3	3	5	3	2	6636.5735	-0.0043
6	3	4	5	3	3	6380.2962	-0.0065
6	4	3	5	4	2	6407.5641	-0.0041
7	1	7	6	1	6	6276.3185	0.0055
7	0	7	6	0	6	6296.1122	0.0058
7	1	6	6	1	5	7248.5162	-0.0024
7	2	5	6	2	4	7949.6715	-0.0003
7	2	6	6	2	5	7000.7957	0.0009
7	3	4	6	3	3	7885.6024	0.0034
7	3	5	6	3	4	7417.2273	-0.0020
7	4	3	6	4	2	7569.4453	-0.0007
7	4	4	6	4	3	7501.8321	-0.0002
7	5	2	6	5	1	7470.4893	-0.0036
7	5	3	6	5	2	7467.1630	0.0112
7	0	7	6	1	6	6261.4272	-0.0114
7	2	6	7	1	7	5225.9802	-0.0007

Table S29 (Continued).

J´	**K_{-1}´**	**K_{+1}´**	**J´´**	**K_{-1}´´**	**K_{+1}´´**	**Obs.**	**Obs.-Cal.**
7	6	1	7	5	2	7913.4357	-0.0051
8	1	8	7	1	7	7119.5287	0.0068
8	0	8	7	0	7	7128.2384	0.0044
8	1	7	7	1	6	8050.8516	0.0004
8	2	7	7	2	6	7893.2903	0.0082
8	1	7	8	1	8	5829.9644	0.0125
8	1	8	7	0	7	7134.3871	-0.0090
9	1	9	8	1	8	7959.9612	0.0056
9	0	9	8	0	8	7963.6308	0.0002

Table S30. Observed rotational transitions and residuals (in MHz) for $^{2}D_{15}$-$^{2}D_{20}$-$^{2}D_{22}$ isotopomers of the T1-w-1 *o*-anisic acid-water complex in the ground vibrational state. See Figure 3 for atom labeling.

J′	**K_{-1}′**	**K_{+1}′**	**J′′**	**K_{-1}′′**	**K_{+1}′′**	**Obs.**	**Obs.-Cal.**
2	1	1	1	1	0	2291.9909	0.0127
3	1	2	2	1	1	3406.5869	-0.0027
4	1	4	3	1	3	3679.9584	-0.0002
4	0	4	3	0	3	3810.3998	-0.0105
4	1	3	3	1	2	4475.2046	-0.0108
4	3	2	4	2	3	3724.5205	-0.0024
4	4	0	4	3	1	4922.8342	0.0115
5	1	4	4	1	3	5472.4796	-0.0031
5	1	4	5	0	5	3029.4369	-0.0070
5	4	1	5	3	2	4811.4426	0.0148
5	5	1	5	4	2	6373.1031	-0.0128
6	1	6	5	1	5	5403.5416	0.0018
6	0	6	5	0	5	5443.2188	0.0025
6	1	5	5	1	4	6380.6076	0.0039
6	2	4	5	2	3	6845.7872	0.0046
6	2	5	5	2	4	6059.4830	0.0044
6	3	3	5	3	2	6634.5620	-0.0091
6	3	4	5	3	3	6366.4372	-0.0139
6	4	2	6	3	3	4596.8656	-0.0089
7	1	7	6	1	6	6247.8746	-0.0003
7	0	7	6	0	6	6266.1665	0.0006
7	1	6	6	1	5	7212.2776	-0.0014
7	2	5	6	2	4	7930.0826	0.0091
7	2	6	6	2	5	6974.2663	0.0029
7	3	4	6	3	3	7884.2421	0.0135
7	3	5	6	3	4	7398.8446	0.0004
7	4	3	6	4	2	7562.1211	-0.0041
7	4	4	6	4	3	7489.1083	-0.0057
8	1	8	7	1	7	7086.8695	0.0011
8	0	8	7	0	7	7094.7902	-0.0006
8	1	7	7	1	6	8009.2014	-0.0072
8	2	7	7	2	6	7860.9189	0.0032
8	2	7	8	1	8	5976.1924	0.0125
9	1	9	8	1	8	7923.2400	0.0029
9	0	9	8	0	8	7926.5285	0.0016
9	2	8	9	1	9	6778.9400	-0.0119
13	4	10	13	3	11	7827.6462	0.0040

Table S31. Observed rotational transitions and residuals (in MHz) for the C2-w-1 conformer of *o*-anisic acid-water complex in the ground vibrational state.

J′	**K$_{-1}$′**	**K$_{+1}$′**	**J′′**	**K$_{-1}$′′**	**K$_{+1}$′′**	**Obs.**	**Obs.-Cal.**
3	1	2	2	1	1	3370.6501	-0.0024
4	1	3	3	1	2	4453.9898	-0.0019
4	0	4	3	0	3	3905.6980	0.0082
4	3	2	3	3	1	4205.7064	0.0077
4	1	4	3	0	3	4183.6796	-0.0061
4	2	3	3	1	2	6202.5827	0.0021
5	1	5	4	1	4	4641.8060	0.0047
5	0	5	4	0	4	4760.9951	0.0116
5	1	4	4	1	3	5495.0099	-0.0084
5	2	3	4	2	2	5564.7618	-0.0084
5	3	3	4	3	2	5267.1679	0.0021
6	1	6	5	1	5	5526.2069	-0.0025
6	0	6	5	0	5	5600.7279	0.0028
6	1	5	5	1	4	6477.4962	0.0060
6	4	2	5	4	1	6336.7564	-0.0007
6	4	3	5	4	2	6328.6504	0.0048
6	1	6	5	0	5	5685.0233	0.0072
6	1	5	5	2	4	5091.6973	-0.0150
7	1	7	6	1	6	6399.7739	0.0056
7	0	7	6	0	6	6441.6045	-0.0013
7	1	6	6	1	5	7392.5115	-0.0057
7	2	6	6	2	5	7060.9079	-0.0143
7	3	5	6	3	4	7372.2648	-0.0078
7	4	4	6	4	3	7405.4164	0.0033
7	0	7	6	1	6	6357.3141	-0.0072
7	1	7	6	0	6	6484.0697	-0.0015
7	2	6	7	1	7	5281.9444	0.0012
8	1	8	7	1	7	7266.1241	0.0013
8	0	8	7	0	7	7287.9681	0.0000
8	2	6	7	2	5	8946.0078	0.0069
8	2	7	7	2	6	7989.6599	0.0001
8	3	5	7	3	4	8869.9069	-0.0066
8	1	8	7	0	7	7308.5943	-0.0024

Table S31 (Continued).

J´	**K_{-1}´**	**K_{+1}´**	**J´´**	**K_{-1}´´**	**K_{+1}´´**	**Obs.**	**Obs.-Cal.**
8	2	7	8	1	8	6005.4745	-0.0015
9	1	9	8	1	8	8128.0632	0.0012
9	0	9	8	0	8	8138.9417	0.0001
9	1	8	8	1	7	9076.5102	-0.0025
9	2	8	8	2	7	8897.0210	0.0015
9	3	7	8	3	6	9409.2969	-0.0005
9	3	7	9	1	8	6246.1231	0.0081
9	2	7	8	3	6	7679.0457	0.0010
10	1	10	9	1	9	8987.5488	0.0004
10	0	10	9	0	9	8992.7869	0.0000
10	1	9	9	1	8	9898.2407	0.0013
10	1	10	9	0	9	8997.3019	-0.0009
11	1	11	10	1	10	9845.7564	0.0001
11	0	11	10	0	10	9848.2152	-0.0006

Table S32. Principal inertial axis coordinates for the atoms of the T1 conformer of *o*-anisic acid. The table compares the theoretical coordinates calculated at the MP2, CCSD and B3LYP-D3 methods with the 6-311++G(d,p) basis set with the experimental r_s and r_m coordinates. The r_s method[34,35] uses the inertial moments of the monosubstituted isotopologues to obtain directly, trough Kraitchman equations, the absolute values of the Cartesian coordinates of the substituted atoms in the principal axis system of the parent molecule. The signs of the r_s coordinates can be taken from any reasonable structure, i.e., one calculated from *ab initio* methods. This method has drawbacks for the determination of atoms near the inertial axes or for light atoms. The mass dependence r_m structure[36] gives equilibrium-quality coordinates and has been used by a least-square fit of the all obtained parameters and implemented in program STRFIT.[i] The $r_m^{(1L)}$ definition was employed. The parameter δ_H for all r_m-r(C-H) bonds was fixed to 0.01 Å. [ii] The different c_α constants of the $r_m^{(1L)}$ method were estimated to have similar values in both cases so in the final fits these were assumed to be equal. In the final fit for T1 conformer the parameters for all the C-H bonds were fixed to the values calculated with the CCSD/6-311++G(d,p) method. See Figure 3 for atom labeling.

[i] Kisiel, Z. Least-Squares Mass-Dependence Molecular Structures for Selected Weakly Bound Intermolecular Clusters. *J. Mol. Spectrosc.* **2003**, 218, 58-67.

[ii] Laurie, V. W. Note on the Determination of Molecular Structure from Spectroscopic Data. *J. Chem. Phys.* **1958**, 28, 704.

atom	method	*a*	*b*	*c* [a]
C1	r_e^{MP2}	-0.4064	0.4689	[0.0000]
	r_e^{CCSD}	-0.4020	0.4707	[0.0000]
	r_e^{DFT}	-0.3997	0.4775	[0.0000]
	$r_m^{(1L)}$	-0.3994(59)[b]	0.4641 (54)	[0.0000]
	r_s	-0.3745 (40)	0.4595 (33)	[0.0000]
C2	r_e^{MP2}	0.6869	-0.4273	[0.0000]
	r_e^{CCSD}	0.6865	-0.4310	[0.0000]
	r_e^{DFT}	0.6860	-0.4247	[0.0000]
	$r_m^{(1L)}$	0.6841 (22)	-0.4237 (25)	[0.0000]
	r_s	0.6764 (22)	-0.4064 (37)	[0.0000]
C3	r_e^{MP2}	2.0009	0.0576	[0.0000]
	r_e^{CCSD}	2.0026	0.0458	[0.0000]
	r_e^{DFT}	1.9994	0.0474	[0.0000]
	$r_m^{(1L)}$	1.9978 (15)	0.0613 (27)	[0.0000]
	r_s	1.99552(75)	[0.0000][c]	[0.0000]
C4	r_e^{MP2}	2.2375	1.4364	[0.0000]
	r_e^{CCSD}	2.2443	1.4244	[0.0000]
	r_e^{DFT}	2.2440	1.4190	[0.0000]
	$r_m^{(1L)}$	2.2323 (13)	1.4291 (21)	[0.0000]
	r_s	2.23051(67)	1.4281 (11)	[0.0000]

[a] *c* coordinates are fixed to zero assuming the planarity of the T1 conformation.

[b] Standard error is given in parentheses in units of the last digits.

[c] r_s parameters in square brackets are fixed to zero owing to the Kraitchman equations give imaginary values or cannot determinate the coordinates.

Table S32 (Continued).

atom	method	*a*	*b*	*c* [a]
C$_5$	r_e^{MP2}	1.1674	2.3344	[0.0000]
	r_e^{CCSD}	1.1821	2.3302	[0.0000]
	r_e^{DFT}	1.1874	2.3248	[0.0000]
	$r_m^{(1L)}$	1.1676 (22)[b]	2.3292 (13)	[0.0000]
	r_s	1.1655 (13)	2.32921(64)	[0.0000]
C$_6$	r_e^{MP2}	-0.1396	1.8455	[0.0000]
	r_e^{CCSD}	-0.1273	1.8453	[0.0000]
	r_e^{DFT}	-0.1174	1.8474	[0.0000]
	$r_m^{(1L)}$	-0.1447 (24)	1.8414 (16)	[0.0000]
	r_s	-0.110 (14)	1.84059(82)	[0.0000]
H$_7$	r_e^{MP2}	2.8428	-0.6245	[0.0000]
	r_e^{CCSD}	2.8410	-0.6405	[0.0000]
	r_e^{DFT}	2.8328	-0.6409	[0.0000]
	$r_m^{(1L)}$	2.8404 (22)	-0.6199 (34)	[0.0000]
	r_s	-	-	-
H$_8$	r_e^{MP2}	3.2621	1.7981	[0.0000]
	r_e^{CCSD}	3.2713	1.7805	[0.0000]
	r_e^{DFT}	3.2689	1.7724	[0.0000]
	$r_m^{(1L)}$	3.2579(17)	1.7892 (27)	[0.0000]
	r_s	-	-	-
H$_9$	r_e^{MP2}	1.3484	3.4049	[0.0000]
	r_e^{CCSD}	1.3687	3.3998	[0.0000]
	r_e^{DFT}	1.3773	3.3911	[0.0000]
	$r_m^{(1L)}$	1.3494 (39)	3.3996 (12)	[0.0000]
	r_s	-	-	-
H$_{10}$	r_e^{MP2}	-0.9920	2.5177	[0.0000]
	r_e^{CCSD}	-0.9738	2.5242	[0.0000]
	r_e^{DFT}	-0.9606	2.5267	[0.0000]
	$r_m^{(1L)}$	-0.9921 (22)	2.5192 (30)	[0.0000]
	r_s	-	-	-
C$_{11}$	r_e^{MP2}	-1.8690	0.0757	[0.0000]
	r_e^{CCSD}	-1.8701	0.0853	[0.0000]
	r_e^{DFT}	-1.8621	0.0945	[0.0000]
	$r_m^{(1L)}$	-1.86315(77)	0.0779 (14)	[0.0000]
	r_s	-1.85656(81)	[0.0000][c]	[0.0000]
O$_{12}$	r_e^{MP2}	0.3932	-1.7713	[0.0000]
	r_e^{CCSD}	0.3872	-1.7709	[0.0000]
	r_e^{DFT}	0.3856	-1.7653	[0.0000]
	$r_m^{(1L)}$	0.3935 (23)	-1.76376(93)	[0.0000]
	r_s	0.3968 (38)	-1.76429(85)	[0.0000]

[a] *c* coordinates are fixed to zero assuming the planarity of the T1 conformation.

[b] Standard error is given in parentheses in units of the last digit.

[c] r_s parameters in square brackets are fixed to zero owing to the Kraitchman equations give imaginary values or cannot determinate the coordinates.

Table S32 (Continued).

atom	**method**	***a***	***b***	***c*** [a]
O13	r_e^{MP2}	-2.1635	-1.2379	[0.0000]
	r_e^{CCSD}	-2.1800	-1.2215	[0.0000]
	r_e^{DFT}	-2.1729	-1.2158	[0.0000]
	$r_m^{(1L)}$	-2.1633 (21)[b]	-1.2312 (17)	[0.0000]
	r_s	-	-	-
O14	r_e^{MP2}	-2.7466	0.9082	[0.0000]
	r_e^{CCSD}	-2.7352	0.9217	[0.0000]
	r_e^{DFT}	-2.7352	0.9259	[0.0000]
	$r_m^{(1L)}$	-2.7345 (17)	0.9077 (23)	[0.0000]
	r_e^{MP2}	-	-	-
H15	r_e^{MP2}	-1.3305	-1.7392	[0.0000]
	r_e^{CCSD}	-1.3640	-1.7395	[0.0000]
	r_e^{DFT}	-1.3594	-1.7505	[0.0000]
	$r_m^{(1L)}$	-1.3425(25)	-1.7438 (20)	[0.0000]
	r_s	-1.3360 (11)	-1.74576(86)	[0.0000]
C16	r_e^{MP2}	1.4759	-2.6983	[0.0000]
	r_e^{CCSD}	1.4563	-2.7110	[0.0000]
	r_e^{DFT}	1.4335	-2.7364	[0.0000]
	$r_m^{(1L)}$	1.4663 (19)	-2.7017 (11)	[0.0000]
	r_s	1.4635 (10)	-2.70130(56)	[0.0000]
H17	r_e^{MP2}	2.0897	-2.5773	0.8975
	r_e^{CCSD}	2.0734	-2.5989	0.8984
	r_e^{DFT}	2.0528	-2.6425	0.8966
	$r_m^{(1L)}$	2.0831 (18)	-2.5879 (17)	0.89845(0)
	r_s	-	-	-
H18	r_e^{MP2}	2.0897	-2.5773	-0.8975
	r_e^{CCSD}	2.0734	-2.5989	-0.8984
	r_e^{DFT}	2.0528	-2.6425	-0.8966
	$r_m^{(1L)}$	2.0831 (18)	-2.5879 (17)	-0.89845(0)
	r_s	-	-	-
H19	r_e^{MP2}	1.0151	-3.6852	[0.0000]
	r_e^{CCSD}	0.9839	-3.6944	[0.0000]
	r_e^{DFT}	0.9362	-3.7044	[0.0000]
	$r_m^{(1L)}$	0.9968 (33)	-3.6865 (12)	[0.0000]
	r_s	-	-	-

[a] *c* coordinates are fixed to zero assuming the planarity of the T1 conformation.

[b] Standard error is given in parentheses in units of the last digits.

[c] r_s parameters in square brackets are fixed to zero owing to the Kraitchman equations give imaginary values or cannot determinate the coordinates.

Table S33. r_s coordinates (Å) of H_{15} atom of C2 conformer compared to the B3LYP-D3/6-311++G(d,p) r_e coordinates for C1 and C2 conformers.

	|***a***|	|***b***|	|***c***|
r_s C2 H_{15}	3.08344(49)[a]	1.3875(11)	[0.0000][b]
r_e C1 H_{15}	3.61045	0.16353	0.17882
r_e C2 H_{15}	3.06108	1.31473	0.28316

[a] Standard error is given in parentheses in units of the last digits.

[b] The Kraitchman equations for this coordinate give imaginary values since the hydrogen atom is close to the *ab* inertial plane.

Table S34. Principal inertial axis coordinates for the atoms of the T1-w-1 conformer of *o*-anisic acid-water complex. The table compares the theoretical coordinates calculated at the MP2 and B3LYP-D3 methods with the 6-311++G(d,p) basis set with the experimental r_s and r_m coordinates. The r_s method[34,35] uses the inertial moments of the monosubstituted isotopologues to obtain directly, trough Kraitchman equations, the absolute values of the Cartesian coordinates of the substituted atoms in the principal axis system of the parent molecule. The signs of the r_s coordinates can be taken from any reasonable structure, i.e., one calculated from *ab initio* methods. This method has drawbacks for the determination of atoms near the inertial axes or for light atoms. The mass dependence r_m structure[36] gives equilibrium-quality coordinates and has been used by a least-square fit of the all obtained parameters and implemented in program STRFIT (Ref. [i] Table S32). The $r_m^{(1L)}$ definition was employed. The parameter δ_H for all r_m-r(C-H) bonds was fixed to 0.01 Å (Ref. [ii] Table S32). The different c_α constants of the $r_m^{(1L)}$ method were estimated to have similar values in both cases so in the final fits these were assumed to be equal. In the final fit for T1 conformer the parameters for all the C-H bonds were fixed to the values calculated with the CCSD/6-311++G(d,p) method. The non-fitted data for T1-w-1 were fixed to the $r_m^{(1L)}$ data of the monomer. See Figure 3 for atom labeling.

atom	method	*a*	*b*	*c*
C_1	r_e^{MP2}	-0.1192	-0.0034	-0.0037
	r_e^{DFT}	-0.1277	-0.0077	-0.0032
	$r_m^{(1L)}$	-0.10364(04)[a]	-0.01334(45)	-0.00341(14)
	r_s	-	-	-
C_2	r_e^{MP2}	1.2876	0.1468	0.0014
	r_e^{DFT}	1.2791	0.1514	0.0012
	$r_m^{(1L)}$	1.28709(14)	0.15475(55)	0.00132(05)
	r_s	-	-	-
C_3	r_e^{MP2}	1.8650	1.4220	0.0032
	r_e^{DFT}	1.8631	1.4176	0.0029
	$r_m^{(1L)}$	1.8458 (11)	1.43889(96)	0.00307(09)
	r_s	-	-	-
C_4	r_e^{MP2}	1.0488	2.5580	-0.0001
	r_e^{DFT}	1.0558	2.5533	-0.0001
	$r_m^{(1L)}$	1.0204 (19)	2.55456(36)	-0.00011(05)
	r_s	-	-	-
C_5	r_e^{MP2}	-0.3415	2.4249	-0.0051
	r_e^{DFT}	-0.3299	2.4339	-0.0043
	$r_m^{(1L)}$	-0.3662 (18)	2.40849(64)	-0.00461(24)
	r_s	-	-	-
C_6	r_e^{MP2}	-0.9153	1.1527	-0.0069
	r_e^{DFT}	-0.9088	1.1704	-0.0059
	$r_m^{(1L)}$	-0.92183(83)	1.1235 (10)	-0.00635(28)
	r_s	-	-	-

[a] Standard error is given in parentheses in units of the last digits.

[b] r_s parameters in square brackets are fixed to zero owing to the Kraitchman equations give imaginary values or cannot determinate the coordinates.

Table S34 (Continued).

atom	method	*a*	*b*	*c*
H$_7$	r_e^{MP2}	2.9419	1.5419	0.0071
	r_e^{DFT}	2.9381	1.5288	0.0063
	$r_m^{(1L)}$	2.9205 (12)[a]	1.5760 (17)	0.00673(24)
	r_s	-	-	-
H$_8$	r_e^{MP2}	1.5099	3.5419	-0.0014
	r_e^{DFT}	1.5220	3.5322	-0.0015
	$r_m^{(1L)}$	1.4700 (26)	3.54420(69)	-0.00153(03)
	r_s	-	-	-
H$_9$	r_e^{MP2}	-0.9798	3.3030	-0.0077
	r_e^{DFT}	-0.9599	3.3146	-0.0064
	$r_m^{(1L)}$	-1.0132 (24)	3.2804 (11)	-0.00693(35)
	r_s	-	-	-
H$_{10}$	r_e^{MP2}	-1.9943	1.0425	-0.0109
	r_e^{DFT}	-1.9863	1.0753	-0.0094
	$r_m^{(1L)}$	-1.99751(73)	0.9805 (18)	-0.01001(43)
	r_s	-	-	-
C$_{11}$	r_e^{MP2}	-0.8461	-1.3273	-0.0061
	r_e^{DFT}	-0.8566	-1.3102	-0.0054
	$r_m^{(1L)}$	-0.83741(94)	-1.33741(98)	-0.00576(21)
	r_s	-	-	-
O$_{12}$	r_e^{MP2}	2.0407	-1.0056	0.0044
	r_e^{DFT}	2.0281	-1.0012	0.0038
	$r_m^{(1L)}$	2.05355(69)	-0.9822 (11)	0.00408(18)
	r_s	-	-	-
O$_{13}$	r_e^{MP2}	-0.1123	-2.4494	-0.0031
	r_e^{DFT}	-0.1330	-2.4387	-0.0029
	$r_m^{(1L)}$	-0.0998 (17)	-2.45983(44)	-0.00309(08)
	r_s	-	-	-
O$_{14}$	r_e^{MP2}	-2.0581	-1.3954	-0.0105
	r_e^{DFT}	-2.0662	-1.3852	-0.0092
	$r_m^{(1L)}$	-2.03942(98)	-1.3924 (18)	-0.00986(37)
	r_s	-	-	-
H$_{15}$	r_e^{MP2}	0.8293	-2.2011	0.0003
	r_e^{DFT}	0.8181	-2.2245	0.0001
	$r_m^{(1L)}$	0.8382 (16)	-2.22180(23)	0.00008(05)
	r_s	0.8045 (19)	-2.21005(68)	[0.0000][b]

[a] Standard error is given in parentheses in units of the last digits.

[b] r_s parameters in square brackets are fixed to zero owing to the Kraitchman equations give imaginary values or cannot determinate the coordinates.

Table S34 (Continued).

atom	method	*a*	*b*	*c*
C$_{16}$	r_e^{MP2}	3.4614	-0.8846	0.0096
	r_e^{DFT}	3.4558	-0.9328	0.0084
	$r_m^{(1L)}$	3.47304(60)[a]	-0.8565 (21)	0.00892(37)
	r_s	-	-	-
H$_{17}$	r_e^{MP2}	3.8015	-0.3621	0.9085
	r_e^{DFT}	3.8183	-0.4246	0.9062
	$r_m^{(1L)}$	3.81454(30)	-0.3323 (24)	0.90848(41)
	r_s	-	-	-
H$_{18}$	r_e^{MP2}	3.8080	-0.3625	-0.8870
	r_e^{DFT}	3.8240	-0.4248	-0.8872
	$r_m^{(1L)}$	3.82069(19)	-0.3325 (24)	-0.88841(41)
	r_s	-	-	-
H$_{19}$	r_e^{MP2}	3.8415	-1.9052	0.0113
	r_e^{DFT}	3.7987	-1.9655	0.0096
	$r_m^{(1L)}$	3.8593 (13)	-1.8768 (24)	0.01037(41)
	r_s	-	-	-
H$_{20}$	r_e^{MP2}	-3.6848	-0.3171	-0.0167
	r_e^{DFT}	-3.6081	-0.3092	-0.0144
	$r_m^{(1L)}$	-3.6225 (89)	-0.2561 (94)	-0.01541(64)
	r_s	-3.57002(42)	-0.3110 (48)	-0.099 (15)
O$_{21}$	r_e^{MP2}	-4.2712	0.4511	-0.0191
	r_e^{DFT}	-4.2286	0.4384	-0.0165
	$r_m^{(1L)}$	-4.28292(73)	0.44757(75)	-0.01776(73)
	r_s	-4.27783(35)	0.4543 (33)	-0.053 (29)
H$_{22}$	r_e^{MP2}	-5.0074	-0.1804	0.5331
	r_e^{DFT}	-5.0029	-0.1305	0.4617
	$r_m^{(1L)}$	-5.0201 (71)	-0.095 (18)	0.496 (21)
	r_s	-	-	-

[a] Standard error is given in parentheses in units of the last digits.

[b] r_s parameters in square brackets are fixed to zero owing to the Kraitchman equations give imaginary values or cannot determinate the coordinates.

Table S35. r_s and r_m geometry parameters (distances in Å and angles in degree) and their comparison with the r_e structures predicted by *ab initio* MP2 and CCSD and DFT B3LYP-D3 methods with the 6-311++G(d,p) basis set for the *ab* plane for the conformer T1 of *o*-anisic acid. A planar skeleton was assumed.

Parameter	r_s	$r_m^{(1L)}$	r_e^{MP2}	r_e^{CCSD}	r_e^{DFT}
r(C_1-C_2)	1.3616(47)[a]	1.4008(79)	1.414	1.413	1.412
r(C_2-C_3)	1.3803(25)	1.4004(36)	1.401	1.400	1.396
r(C_3-C_4)	1.4473(10)	1.3878(39)	1.399	1.399	1.393
r(C_4-C_5)	1.3951(14)	1.3942(27)	1.397	1.396	1.392
r(C_5-C_6)	1.366 (13)	1.4000(31)[b]	1.395	1.396	1.389
r(C_1-C_6)	1.4061(42)	1.4006(57)[b]	1.402	1.402	1.399
r(C_1-C_{11})	1.5516(40)	1.5138(57)	1.515	1.518	1.512
r(C_2-O_{12})	1.3864(38)	1.3712(30)	1.376	1.373	1.374
r(C_{11}-O_{13})	-	1.3431(22)[b]	1.346	1.343	1.347
r(C_{11}-O_{14})	-	1.2033(23)[b]	1.209	1.203	1.206
r(O_{12}-H_{15})	1.7329(39)	1.7360(34)[b]	1.724	1.752	1.745
r(O_{12}-C_{16})	1.4198(30)	1.4250(29)	1.425	1.423	1.429
r(O_{13}-H_{15})	-	0.9677(33)	0.972	0.966	0.973
∠(C_1-C_2-C_3)	123.4(3)	120.4(3)[b]	120.4	120.4	120.5
∠(C_2-C_3-C_4)	116.5(2)	120.0(2)[b]	120.0	119.9	119.9
∠(C_3-C_4-C_5)	120.89(7)	120.5(2)	120.3	120.5	120.5
∠(C_4-C_5-C_6)	118.8(2)	119.4(2)	119.5	119.2	119.3
∠(C_1-C_6-C_5)	121.8(8)	120.9(3)[b]	121.5	121.6	121.7
∠(C_2-C_1-C_6)	118.6(6)	118.8(4)[b]	118.4	118.3	118.1
∠(C_2-C_1-C_{11})	123.3(3)	125.9(4)[b]	125.6	125.7	125.6
∠(C_6-C_1-C_{11})	118.1(6)	115.3(5)	116.0	116.0	116.3
∠(C_1-C_2-O_{12})	117.8(3)	117.1(3)[b]	117.0	117.0	117.1
∠(C_3-C_2-O_{12})	118.8(3)	122.5(2)[b]	122.6	122.5	122.4
∠(C_1-C_{11}-O_{13})	-	117.7(3)	117.7	118.0	118.0
∠(C_2-O_{12}-C_{16})	119.7(3)	118.9(1)	118.2	118.7	120.2
∠(C_2-O_{12}-H_{15})	101.0(2)	101.6(1)[b]	101.3	101.6	102.1
∠(C_{11}-C_1-C_2-C_3)	180.00000(0)	180.00000(0)[b]	180.0	180.0	180.0
∠(C_{11}-C_1-C_6-C_5)	180.00000(0)	180.00000(1)[b]	180.0	180.0	180.0
∠(O_{12}-C_2-C_1-C_6)	180.00000(0)	180.00000(1)[b]	180.0	180.0	180.0
∠(O_{12}-C_2-C_3-C_4)	180.00000(0)	180.00000(0)[b]	180.0	180.0	180.0
∠(H_{15}-O_{12}-C_2-C_1)	0.00000(1)	0.00000(1)[b]	0.0	0.0	0.0
∠(H_{15}-O_{12}-C_2-C_3)	180.00000(1)	180.00000(0)[b]	180.0	180.0	180.0
∠(C_{16}-O_{12}-C_2-C_1)	180.00000(0)	180.00000(1)[b]	180.0	180.0	180.0
∠(C_{16}-O_{12}-C_2-C_3)	0.00000(0)	0.00000(0)[b]	0.0	0.0	0.0
∠(H_{18}-C_{16}-O_{12}-H_{17})	-	118.7(1)[b]	118.7	118.6	118.6
C_α[c] / $u^{1/2} \cdot$ Å		0.03656(21)			
δ_H / $u^{1/2} \cdot$ Å		[0.010][d]			
σ_{fit}[e] / u · Å^2		0.006662			

[a] Standard error is given in parentheses in units of the last digits.

[b] Derived parameters.

[c] Fitted using the assumption $C_\alpha = C_a = C_b = C_c$.

[d] Fixed values.

[e] Standard deviation of the fit of all the planar moments of inertia.

Table S36. r_s and r_m geometry parameters (distances in Å and angles in degree) and their comparison with the r_e structures predicted by *ab initio* MP2 and DFT B3LYP-D3 methods with the 6-311++G(d,p) basis set for the conformer T1-w-1 of *o*-anisic acid water complex. For the r_m fit the structure of *o*-anisic acid were fixed to T1 conformer r_m values (see Table S35) and the water parameters to the previously determined r_0 values [Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. Molecular Structures of Gas-Phase Polyatomic Molecules Determined by Spectroscopic Methods. *J. Phys. Chem. Ref. Data* 1979, 8, 619-721.]

Parameter	$\mathbf{r_s}$	$\mathbf{r_m^{(1L)}}$	$\mathbf{r_e}$ $^{\mathbf{MP2}}$	$\mathbf{r_e}$ $^{\mathbf{DFT}}$
r(O_{14}-H_{20})		1.9487(19)	1.952	1.880
r(H_{10}-O_{21})		2.3467(11)^b	2.352	2.331
r(H_{20}-O_{21})	1.0435(45)^a	[0.965]^c	0.966	0.972
r(O_{14}-O_{21})		2.9015(16)^b	2.882	2.829
∠(C_{11}-O_{14}-H_{20})		141.7(4)	143.2	141.5
∠(O_{14}-H_{20}-O_{21})		168.8(1.1)	160.9	164.6
∠(C_{11}-O_{14}-H_{20}-O_{21})		[0.0]^c	[0.0]^c	[0.0]^c
∠(O_{14}-H_{20}-O_{21}-H_{22})		146.4(1.6)	143.4	148.7
C_α^d/ $u^{1/2}$ · Å		0.0451(28)		
δ_H / $u^{1/2}$ · Å		[0.010]		
σ_{fit}^e / u · Å^2		0.07471		

[a] Standard error is given in parentheses in units of the last digits.

[b] Derived parameters.

[c] Parameters in square were fixed.

[d] Fitted using the assumption $C_\alpha = C_a = C_b = C_c$.

[e] Standard deviation of the fit of all the planar moments of inertia.

Table S37. B3LYP-D3/6-311++G(d,p) predicted structural relaxation parameters (distances in Å and angles in degree) for some selected bond distances and angles along the coordinate τ ($\tau = \angle C_2C_1C_{11}O_{13} - 90^o$). The variation of these parameters can be described by a periodical function: $\mathbf{P(\tau) = P(0) + P(1)/2 \cdot (1 - sin\tau) + P(2)/2 \cdot (1 - cos2\tau) + P(3)/2 \cdot (1 - sin3\tau) + P(4)/2 \cdot (1 - cos4\tau) + P(5)/2 \cdot (1 - sin5\tau)}$. Values used in the flexible Meyer method to evaluate the potential energy function.

Parameter	**P(0)**	**P(1)**	**P(2)**	**P(3)**	**P(4)**	**P(5)**
r(C_{11}-C_1)	1.5004	-0.0034	-0.0100	0.0010	-0.0033	-0.0002
r(O_{12}-C_2)	1.3627	-0.0040	-0.0110	-	-	-
r(O_{13}-C_{11})	1.3464	0.0169	0.0066	-0.0014	-	-
r(O_{14}-C_{11})	1.2070	-0.0060	0.0061	-	-	-
∠(C_{11}-C_1-C_6)	119.06	3.78	-2.80	-0.86	-0.68	-0.21
∠(O_{12}-C_2-C_1)	115.70	-0.27	2.49	0.11	-0.04	-
∠(O_{13}-C_{11}-C_1)	113.14	-3.22	1.90	0.56	-0.26	-
∠(O_{14}-C_{11}-C_1)	123.64	3.63	0.15	-0.59	-0.10	-
∠(C_{16}-O_{12}-C_2)	118.83	0.11	0.71	0.04	-0.07	-