

Supporting Information

for

Formation of citrazinic acid ions and their contribution to optical and magnetic features: a combined experimental and computational approach.

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Content:

details on the calculation of solvation free energy and pKa

The starting data are the sum of electron and thermal energies (E_{TE}) for the molecules of a defined thermodynamic cycle in gaseous phases and with implicit solvent. Taking cycle 1 in Figure 1 as an example, ΔG_{solv} is the difference between the energy in solvent and the one in gaseous phase for each species.

$$\Delta G_{solv}(CZA) = E_{TE}(CZA_{solv}) - E_{TE}(CZA_{gas})$$

$$\Delta G_{solv}(CZA^-) = E_{TE}(CZA^-_{solv}) - E_{TE}(CZA^-_{gas})$$

ΔG_g is the difference between the two pairs of gas molecules on top of the cycle

$$\Delta G_g(CZA^-) = E_{TE}(CZA^-_{gas}) + E_{TE}(H_3O^+_{gas}) - E_{TE}(CZA_{gas}) - E_{TE}(H_2O_{gas})$$

Finally, ΔG_{sol} is the difference between the calculated terms including the experimental values of ΔG_g for H_2O and H_3O^+

$$\Delta G_{sol} = \Delta G_g(CZA^-) + \Delta G_s(CZA^-) + \Delta G_s(H_3O^+) - \Delta G_s(CZA) - \Delta G_s(H_2O)$$

From the value of ΔG_{sol} one can retrieve the pK_a value

$$pK_a = \frac{\Delta G_{sol}}{1.364} - \log|H_2O| - c$$

where c is a correction value (Chemical Physics Letters 367, 145–149, 2003)

Figure S1: calculated absorption spectra for the CZA+CZA1MA (a) and CZA+CZA1M (b) equilibria

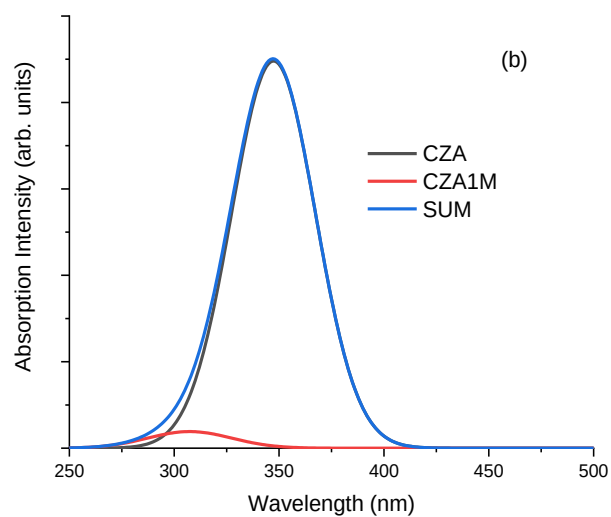
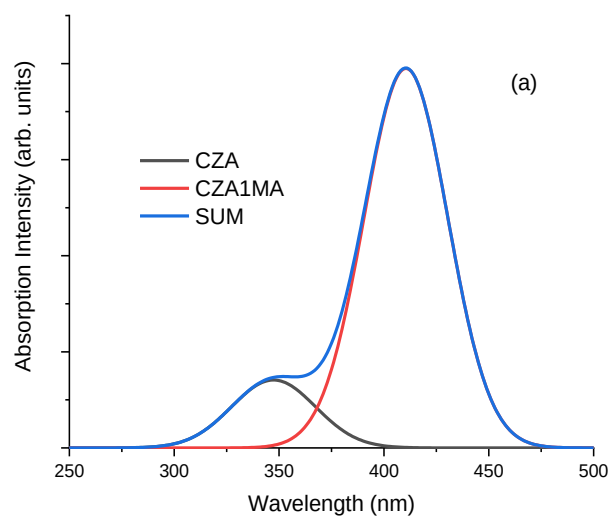
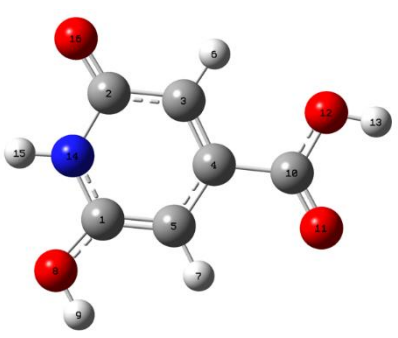
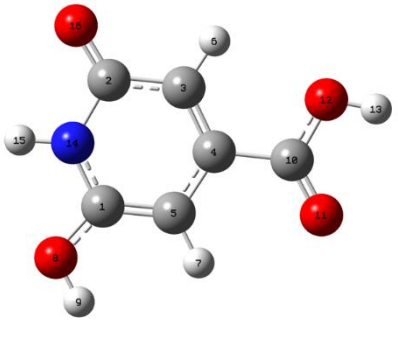
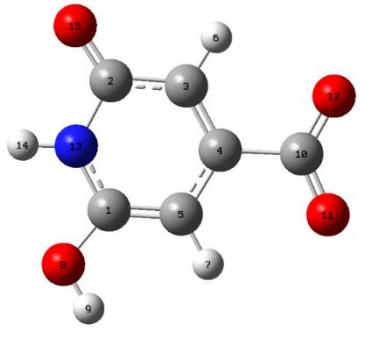
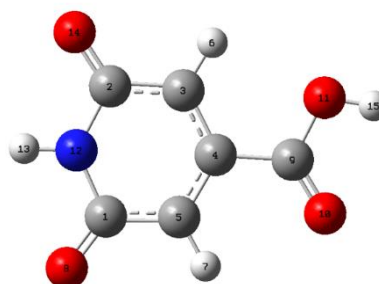


Table S1: GIAO isotropic Magnetic Shielding in water or dmso for CZA, its conjugated bases, its most stable dimer, and CZA+1 DMSO molecule.

GIAO isotropic Magnetic Shielding (ppm) for CZA calculated at the B3LYP/6311++G(d,p)/PCM(water)//B3LYP/6311++G(d,p)/PCM(water)	
C 1 20,9605 C 2 15,2677 C 3 64,6028 C 4 35,0474 C 5 93,2965 H 6 25,1253 H 7 25,837 O 8 197,9442 H 9 26,3272 C 10 10,844 O 11 -73,6314 O 12 125,5298 H 13 25,2102 N 14 73,9744 H 15 23,7799 O16 -7,1832	
GIAO isotropic Magnetic Shielding (ppm) for CZA calculated at the B3LYP/6311++G(d,p)/PCM(dmso)//B3LYP/6311++G(d,p)/PCM(dmso)	
C 1 20,997 C 2 15,3209 C 3 64,5291 C 4 35,0844 C 5 93,3851 H 6 25,1236 H 7 25,8441 O 8 198,0302 H 9 26,3448 C 10 10,858 O 11 -73,8662 O 12 125,5311 H 13 25,2209 N 14 74,0423 H 15 23,7886 O 16 -8,021	
GIAO isotropic Magnetic Shielding (ppm) for CZA1M calculated at the B3LYP/6311++G(d,p)/PCM(dmso)//B3LYP/6311++G(d,p)/PCM(dmso)	
C 1 22,8151 C 2 14,2285 C 3 69,1661 C 4 21,3045 C 5 91,767 H 6 25,3047 H 7 25,6895 O 8 203,6326 H 9 26,7276 C 10 10,161 O 11 7,1694 O 12 19,2876 N 13 78,568 H 14 24,1195 O 15 17,9207	

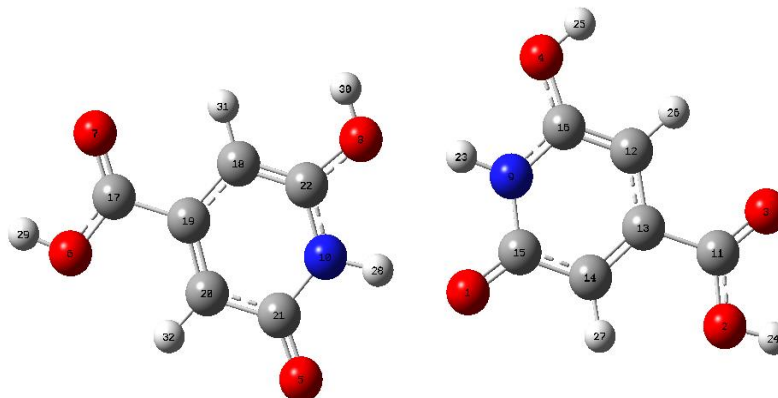
GIAO isotropic Magnetic Shielding (ppm) for CZA1MA calculated at the B3LYP/6311++G(d,p)/PCM(dmso) //B3LYP/6311++G(d,p)/PCM(dmso)

C 1	11,8046
C 2	11,2729
C 3	85,1613
C 4	36,0027
C 5	85,3718
H 6	26,2033
H 7	26,241
O 8	40,1518
C 9	7,332
O 10	-58,5163
O 11	122,9345
N 12	55,5363
H 13	24,4421
O 14	37,9213
H 15	25,6173



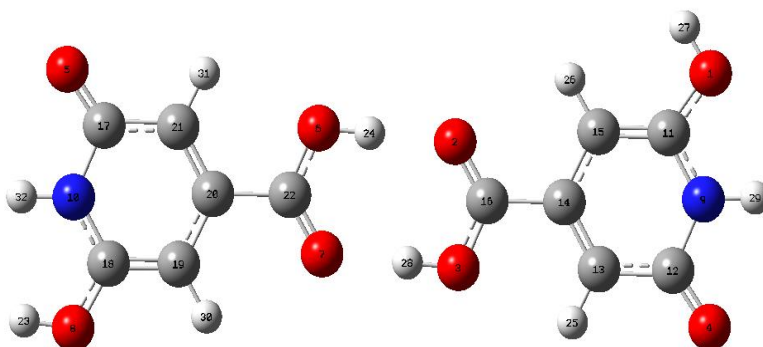
GIAO isotropic Magnetic Shielding (ppm) for CZA head to head dimer calculated at the ω B97XD/6-311++G(d,p)/PCM(dmso) //B3LYP/6311++G(d,p)/PCM(dmso)

O 1	16,2372
O 2	130,2828
O 3	-66,111
O 4	200,4352
O 5	-4,1443
O 6	130,9134
O 7	-65,3002
O 8	202,6725
N 9	75,9163
N 10	70,4327
C 11	13,3488
C 12	92,9917
C 13	34,9026
C 14	66,1651
C 15	14,7734
C 16	22,425
C 17	12,5301
C 18	95,4612
C 19	36,7016
C 20	63,8339
C 21	15,2587
C 22	22,3147
H 23	21,2424
H 24	25,3061
H 25	26,4289
H 26	25,7355
H 27	25,034
H 28	18,4729
H 29	25,3749
H 30	26,2763
H 31	25,8519
H 32	25,1208



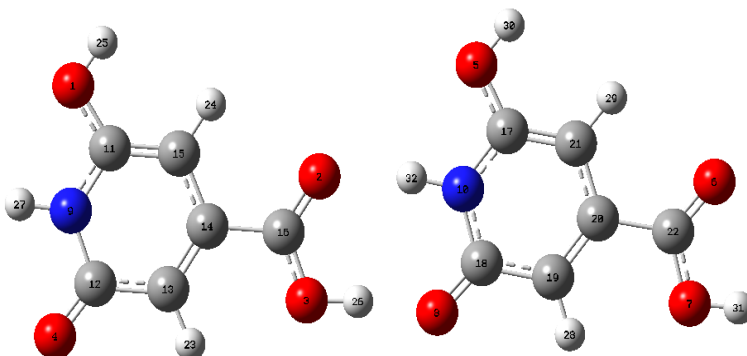
GIAO isotropic Magnetic Shielding (ppm) for CZA tail to tail dimer calculated at the ω B97XD/6-311++G(d,p)/PCM(dmso) //B3LYP/6311++G(d,p)/PCM(dmso)

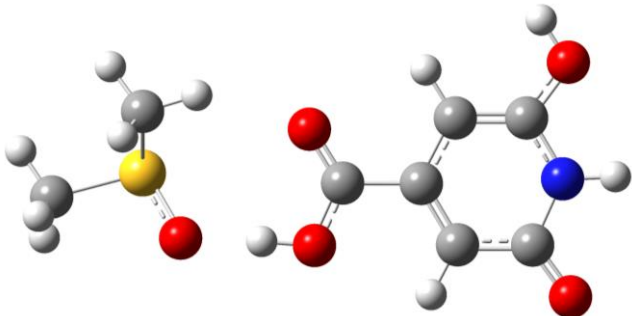
O 1 200,8223
O 2 -28,6683
O 3 115,2515
O 4 -4,7398
O 5 -3,9212
O 6 115,1431
O 7 -28,9122
O 8 201,4582
N 9 76,5467
N 10 74,4777
C 11 22,4126
C 12 16,8298
C 13 65,0224
C 14 34,8483
C 15 95,4228
C 16 6,2634
C 17 16,7599
C 18 23,3393
C 19 93,5104
C 20 34,2529
C 21 66,2619
C 22 6,3085
H 23 27,0403
H 24 18,5218
H 25 25,0735
H 26 25,8261
H 27 26,4969
H 28 18,4751
H 29 23,8887
H 30 25,6894
H 31 25,1003
H 32 24,1521



GIAO isotropic Magnetic Shielding (ppm) for CZA head to tail dimer calculated at the ω B97XD/6-311++G(d,p)/PCM(dmso) //B3LYP/6311++G(d,p)/PCM(dmso)

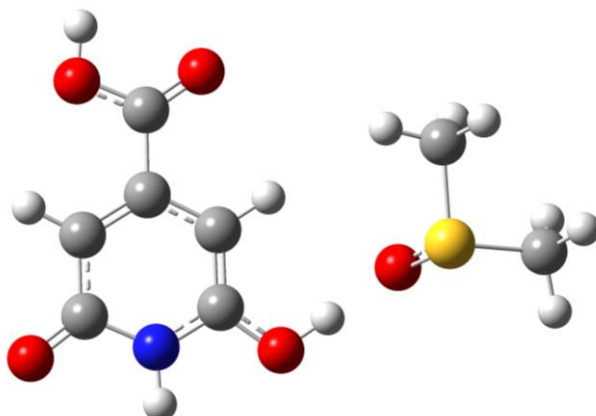
O 1 201,5907
O 2 -38,9228
O 3 108,8461
O 4 -1,5128
O 5 199,2388
O 6 -66,7959
O 7 130,2512
O 8 43,6046
N 9 77,2334
N 10 72,6617
C 11 22,603
C 12 16,8182
C 13 65,6382
C 14 33,4132
C 15 95,0634
C 16 7,5609
C 17 21,9188
C 18 13,5205
C 19 67,3309
C 20 34,5036
C 21 91,4607
C 22 12,9858
H 23 25,0876
H 24 25,7584



H 25 26,5322 H 26 16,6472 H 27 23,8962 H 28 25,0984 H 29 25,6239 H 30 26,3794 H 31 25,2817 H 32 18,7653	
GIAO isotropic Magnetic Shielding (ppm) for CZA + DMSO system, with DMSO molecule near the carboxylic group, calculated at the ωB97XD/6311++G(d,p)/PCM(dms)//B3LYP/6311++G(d,p)/PCM(dms)	
C 1 22,8587 C 2 95,3699 N 3 77,723 O 4 202,2792 C 5 32,7393 C 6 10,0447 O 7 -53,2107 O 8 109,9285 H 9 17,6384 H 10 26,5952 C 11 16,4198 H 12 23,9761 O 13 1,0371 C 14 66,6411 H 15 25,1925 H 16 25,8873 S 17 182,2015 C 18 142,5282 C 19 141,0162 H 20 29,6803 H 21 29,4594 H 22 29,2623 H 23 28,6886 H 24 29,6379 H 25 29,7107 O 26 265,7563	

GIAO isotropic Magnetic Shielding (ppm) for CZA + DMSO system, with DMSO molecule near the hydroxyl group, calculated at the ω B97XD/6311++G(d,p)/PCM(dmso)//B3LYP/6311++G(d,p)/PCM(dmso)

C 1	21,248
C 2	95,3968
N 3	67,8963
O 4	201,1025
C 5	36,6728
C 6	12,12
O 7	-64,1792
O 8	130,6485
H 9	25,4269
H 10	26,6834
C 11	14,5089
H 12	18,2114
O 13	0,9035
C 14	65,6305
H 15	25,2465
H 16	25,9407
S 17	181,8258
C 18	141,4873
C 19	140,8071
H 20	29,6832
H 21	29,2578
H 22	29,494
H 23	29,6803
H 24	29,7337
H 25	28,2723
O 26	262,6697



GIAO isotropic Magnetic Shielding (ppm) for CZA + DMSO system, with DMSO molecule near the NH group, calculated at the ω B97XD/6311++G(d,p)/PCM(dmso)//B3LYP/6311++G(d,p)/PCM(dmso)

C 1	19,238
C 2	94,5672
N 3	73,3525
O 4	174,9715
C 5	35,9487
C 6	11,8458
O 7	-64,2641
O 8	130,272
H 9	25,4633
H 10	18,4404
C 11	16,044
H 12	24,0162
O 13	5,8062
C 14	69,3658
H 15	25,3935
H 16	25,6217
S 17	180,5515
C 18	141,1065
C 19	141,506
H 20	29,6371
H 21	29,075
H 22	29,3627
H 23	29,3852
H 24	29,658
H 25	29,2278
O 26	259,378

