Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

A theoretical investigation of the low energy conformers of the neutral and zwitterionic glycine and methylcarbamic acid in water clusters and their role in the interstellar medium

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Supplementary Material

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Comparison of low energy neutral and zwitterionic glycine conformers described in this paper with those obtained previously with other computational methods.

As noted in the introduction, there have been many previous studies on the relative energies of different glycine conformers in water clusters. Because of the small energy differences between the different conformers, different computational methods give slightly different energy ordering to the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) methods we use. Below we summarize how the energy ordering for some of the Aikens and Gordon[46], and the Bachrach[47] glycine conformers differ from our results.

GlyW2: The lowest energy zwitterionic glycine structures previously found by Aikens and Gordon (structure 2Z-a in Fig 2) at RHF/6-31++G(d,p) level and by Bachrach (structure Z2-a in Fig 3) at PBE1PBE/6-311+G(d,p) level is similar to zGlyW2a structure in Fig 2, except that it has both a water molecule and the $-NH_3^+$ group hydrogen bonding to the same oxygen in the $-CO_2^-$ group. We also found this to be the lowest energy structures in our preliminary B3LYP/6-311++G(d,p) calculations and is listed as the zGlyW2e structure in the Supplementary Material. However, reoptimization of the zGlyW2e conformer at the MP2/6-311++G(d,p) level resulted in a spontaneous transfer of a proton from the $-NH_3^+$ to the $-CO_2^-$ group to produce the neutral glycine form indicating that the lowest energy glycine zwitterion structures previously found by Aikens and Gordon, and Bachrach are not stable at the MP2/6-311++G(d,p) level of theory.

GlyW3: The most stable zwitterionic conformer, zGlyW3a is 33.9 kJ mol^{-1} less stable than nGlyW3a. The previous structures reported by Aikens and Gordon at RHF/6-311++G(d,p) level and also by Bachrach using PBE1PBE/6-311+G(d,p) found our nGlyW3c structure to have the lowest energy. It is worth noting that the first three lowest energy MP2/6-311++G(d,p) conformers are very close in energy, differing by only 1.7 kJ mol^{-1}; and as listed in the supplementary material, we also find the nGlyW3c structure to be the lowest energy B3LYP/6-311++G(d,p) structure.

GlyW4: Both our nGlyW4a and the zGlyW4a structures correspond to the lowest energy neutral and zwitterionic glycine conformers (4N6-a and 4Z-a) previously found by Aikens and Gordon in their MP2/6-31++g(d,p)//RHF/6-31++G(d,p) calculations, but their 11 kJ mol^{-1} energy difference is smaller than the 21.7 kJ mol^{-1} we find.

GlyW5: Our preliminary B3LYP calculations found Bachrach's lowest energy N5-a structure to be the lowest energy neutral nMCAW5 cluster, reoptimization at the MP2 level shifted this to being the sixth lowest energy at 10.6 kJ mol^{-1}, and hence, it is not included in Fig 5 and Table 2. The two lowest MP2/6-311++G(d,p) energy structures found in our study, nGlyW5a and nGlyW5b, match with the 5N6-a and 5N8-a structures, respectively, obtained by Aikens and

Gordon. The zGlyW5a structure corresponds to Bachrach's second lowest energy zwitterionic complex, Z5-b, and his Z-5a cluster is our second lowest energy zwitterion cluster.

GlyW6: Our MP2 level calculations give the same lowest energy neutral and zwitterionic structures as previously found by Aikens and Gordon (6N6-a and 6Z-a, respectively).[46] Whereas, we found the Bachrach lowest energy neutral structure, N6-a, to correspond to our third low energy structure, nGlyW6c, and his zwitterionic lowest energy structure, Z6-a, to be our second zwitterion, zGlyW6b.

GlyW7: Our preliminary B3LYP/6-311++G(d,p) calculations on the seven water clusters gave nGlyW7c as the lowest energy structure in agreement with the 7N1-a structure found by Aikens and Gordon in their RHF/6-31++G(d,p) calculations. However, reoptimization at the MP2/6-311++G(d,p) level found this structure to have the third lowest energy, and instead our lowest energy nGlyW7a structure corresponds to the Aikens and Gordon 7N6-a structure. Likewise, Aikens and Gordon's lowest energy zwitterionic structure (7Z-f at RHF/6-311++G(d,p) level) turned out to be our third lowest energy zGlyW7c conformer. While our lowest energy zwitterion, zGlyW7a, corresponds to the lowest energy Z7-a structure found by Bachrach. It should be noted that Aikens and Gordon's RHF/6-31++G(d,p) calculations found the zwitterionic 7Z-f structure (zGlyW7c in this study) to be around 35 kJ mol^{-1} less stable than their lowest energy neutral structure 7N1-a (nGlyW7c), whereas their single point MP2/6-31++G(d,p)//RHF/6-31++G(d,p) calculations changed this ordering completely and gave the zwitterionic 7Z-b (zGlyW7b) cluster as the lowest energy structure at just 1.3 kJ mol^{-1} more stable than the lowest energy neutral complex 7N8-a (nGlyW7b). Bachrach with PBE1PBE/6-311+G(d,p) calculations found the lowest energy neutral and zwitterionic glycine clusters with seven waters to be isoenergetic. However, our MP2/6-311++G(d,p) calculations on Bachrach lowest energy neutral conformer, N7-a, gives only our fifth lowest energy nGlyW7e structure. Interestingly, like Bachrach we also find the nGlyW7e structure to be isoenergetic with the lowest energy zwitterion structure zGlyW7a with both structures being 8.3 kJ mol^{-1} above the lowest energy neutral glycine nGlyW7a conformer.

GlyW8: For the clusters containing eight waters, we reoptimized the geometries the structures previously reported by Aikens and Gordon. Since there were only 4 structures reported previously for the zwitterionic form we also generated some additional new structures as explained in the Computational Method.

Table S1. Relative energies (in kJ mol^{-1}) of neutral and zwitterionic conformers of glycine and methylcarbamic acid with 1 to 10 water molecules at the B3LYP/6-311++G(d,p) level. The molecules are arranged in this table by the order of their increasing MP2/6-311++G(d,p) optimized energies given in tables 1 and 2 of the main paper.

	Number of water molecules Wx									
Molecule	1	2	3	4	5	6	7	8	9	10
nMCA•Wxa	0.0	0.0	0.0	0.0	3.0	0.0	0.0	0.0	0.0	2.1
nMCA•Wxb	3.9	3.6	3.5	5.2	4.6	6.6	1.6	2.7	0.0	0.0
nMCA•Wxc	11.5	13.2	9.8	2.8	0.0	5.9	0.8	11.7	1.1	5.1
nMCA•Wxd	16.1	16.0	7.8	3.9	7.6	14.1	2.5	12.6	10.4	4.8
zMCA•Wxa	-	61.2	54.7	48.5	59.3	44.8	42.2	41.2	42.9	38.8
zMCA•Wxb	-	61.5	54.3	50.4	52.0	53.5	42.7	58.3	49.4	40.2
zMCA•Wxc	-	64.3	56.4	73.6	65.3	55.7	53.8	60.5	52.3	42.4
zMCA•Wxd	-	-	57.5	69.4	66.2	61.3	55.3	68.1	53.5	51.9
nGly•Wxa	43.4	42.8	52.7	44.5	45.4[b]	39.5	33.6	45.3	44.2	46.4
nGly•Wxb	49.0	44.5	54.0	45.0	50.0	40.1	31.5	50.2	51.6	40.2
nGly•Wxc	48.1	47.9	43.2	47.5	48.9	45.0	29.7	47.3	54.0	42.8
nGly•Wxd	52.4	48.7	47.4	50.0	48.9	45.8	41.3	50.3	53.7	47.4
zGly•Wxa	-	98.8[a]	84.6	70.7	63.9	53.2	41.2	54.2	47.6	37.8
zGly•Wxb	-	102.5	83.1	70.8	62.3	52.6	38.6	52.2	47.3	37.3
zGly•Wxc	-	102.6	83.6	72.4	62.7	55.1	46.3	50.4	55.5	40.4
zGly•Wxd	-	104.6	84.0	74.6	65.7	56.8	44.0	71.0	66.5	40.3

[a] The most stable zwitterionic glycine structure at the B3LYP/6-311++G(d,p) level is zGlyW2e with a relative energy of 94.8 kJ mol^{-1} which is not a stable structure at the MP2/6-311++G(d,p) level. The structure is given in Fig S1.

[b] The most stable neutral glycine structure at the B3LYP/6-311++G(d,p) level is nGlyW5e with a relative energy of 43.9 kJ mol^{-1} which is the fifth lowest energy neutral glycine structure at the MP2/6-311++G(d,p) level. The structure is given in Fig S1.

Table S2. Relative energies (in kJ mol^{-1}) of neutral and zwitterionic glycine conformers with 1 to 10 water molecules at the B3LYP/6-311++G(d,p) level. The molecules are arranged in this table by the order of their increasing MP2/6-311++G(d,p) optimized energies given in tables 1 and 2 of the main paper.

	Number of water molecules Wx									
Molecule	1	2	3	4	5	6	7	8	9	10
nGly•Wxa	0.0	0.0	9.5	0.0	1.5[b]	0.0	3.9	0.0	0.0	9.1
nGly•Wxb	5.8	1.7	10.8	0.6	6.1	0.6	1.8	4.8	7.5	3.0
nGly•Wxc	4.9	5.1	0.0	3.1	5.1	5.5	0.0	2.0	9.8	5.5
nGly•Wxd	9.1	5.9	4.1	5.3	5.0	6.4	11.6	5.0	9.5	10.2
zGly•Wxa	-	56.0[a]	41.4	26.3	20.0	13.7	11.5	8.9	3.5	0.5
zGly•Wxb	-	59.7	39.9	26.4	18.4	13.2	8.9	6.9	3.1	0.0
zGly•Wxc	-	59.8	40.4	28.0	18.8	15.7	16.6	5.0	11.3	3.1
zGly•Wxd	-	61.8	40.7	30.1	21.8	17.4	14.3	25.6	22.4	3.0

[a] The most stable zwitterionic glycine structure at the B3LYP/6-311++G(d,p) level is zGlyW2e with a relative energy of 51.9 kJ mol^{-1} which is not a stable structure at the MP2/6-311++G(d,p) level. The structure is given in Fig S1.

[b] The most stable neutral glycine structure at the B3LYP/6-311++G(d,p) level is nGlyW5e which is the fifth lowest energy neutral glycine structure at the MP2/6-311++G(d,p) level. The structure is given in Fig S1.

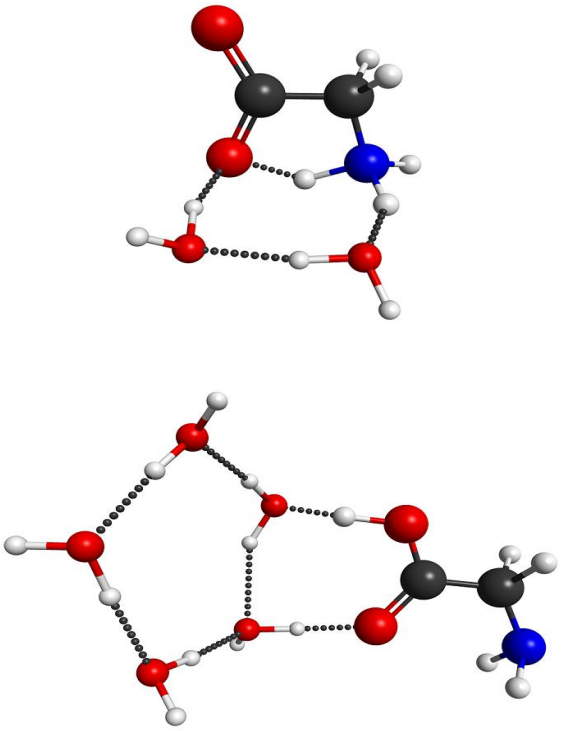

Fig S1. Structures of the zGlyW2e and nGlyW5e configurations obtained by B3LYP/6-311++G(d,p).

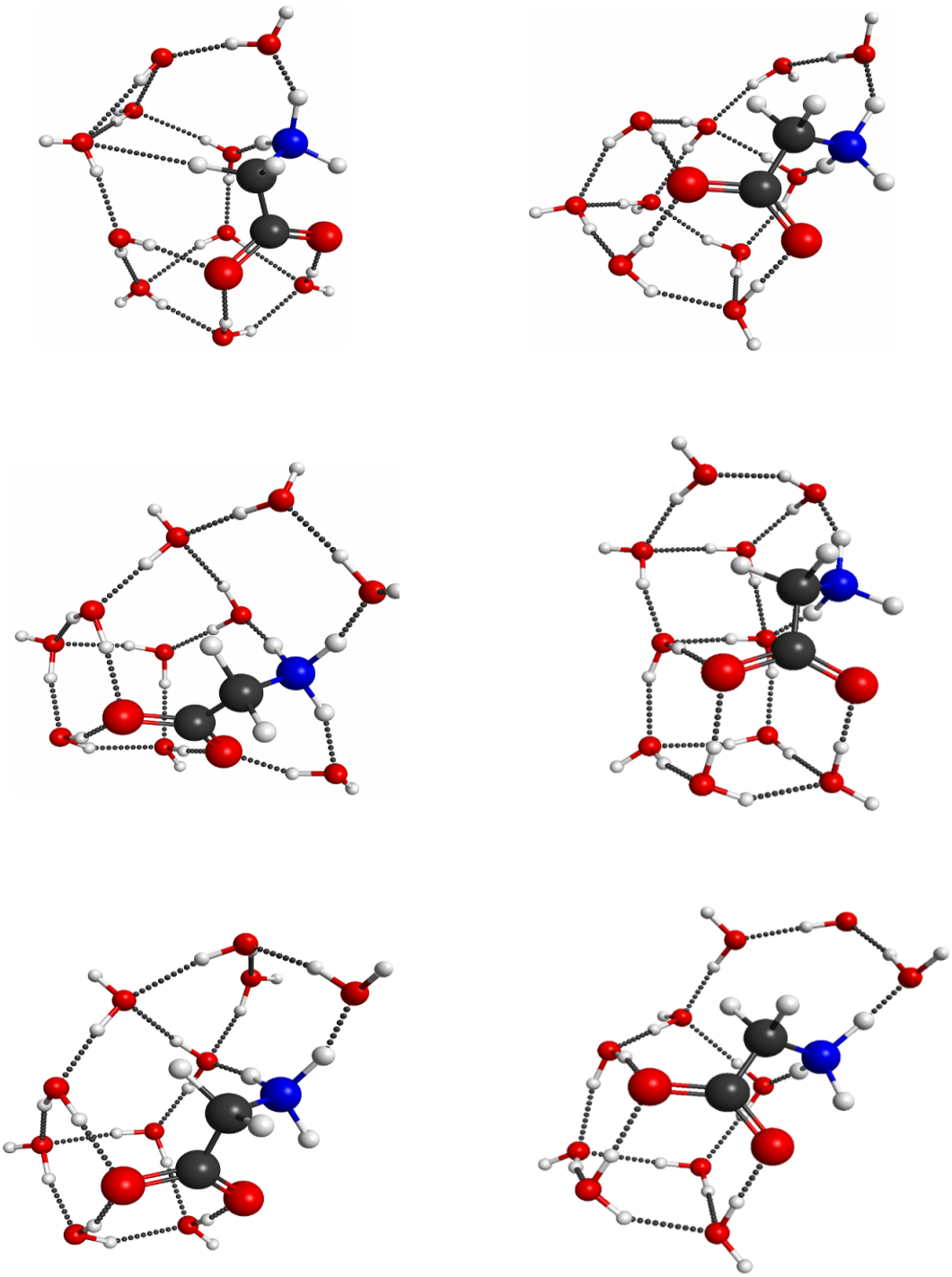

Fig S2. The six of the lowest energy zwitterionic glycine structures, which are more stable than the lowest energy neutral glycine conformer, nGlyW10a, by 11.0, 9.0, 7.9 (in column 1), 6.3, 6.0 and 4.1 kJ mol^{-1} (in column 2), respectively, obtained by the MP2/6-311++G(d,p) calculations.