**Structural elucidation, theoretical insights and thermal properties of three novel multicomponent molecular forms of gallic acid with hydroxypyridines**

Jyothi K. La,b, Karthik Kumaraa, Hema M. K.a, Maheshaa, Raj Gautamc, Guru Row T. N.c and Lokanath N. K.a\*

a Department of Studies in Physics, Manasagangotri, University of Mysore, Mysuru 570006, India.

b Department of Physics, Government First Grade College and PG Centre, Chintamani 563125, India.

c Solid State and Structural Chemistry Unit, Indian Institute of Science, Bengaluru 560012, India.

**Supplementary information**

**Table S1**. FTIR major bands (in cm-1) assignment of starting and multicomponent compounds.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | νO-H  (Alcohol) | νO-H  (Acid) | νC=O  (Acid) | νC-O  (Acid) | ν N-H  (Bending) | νN-H  (Stretching) |
| GA | 3345.27 | 3273.45 | 1700.25 | 1239.40 | -- | -- |
| 2HP | 3070.15 | -- | -- | -- | 1638.19 | -- |
| 3HP | 3062.56 | -- | -- | -- | 1590.35 | -- |
| 4HP | 3421.39 | -- | -- | -- | 1638.27 | -- |
| GA-2HP | 3258.06 | 2984.27 | 1742.15 | 1299.92 | 1645.94 | 3413.61 |
| GA-3HP | 3072.92 | 2521.67 | 1336.94 | | 1617.95 | 3510.35 |
| GA-4HP | 3091.49 | 2982.89 | 1700.00 | 1341.66 | 1635.45 | 3462.38 |

**Table S2.** Interatomic distances (Å), bond angles () and symmetry codes of inter/intra molecular hydrogen bonds.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **GA-2HP cocrystal** | | | | | |
| **D-H...A** | **D-H** | **H...A** | **D...A** | **D-H...A** | **Symmetry Code** |
| O9-H9…O19 | 0.82 | 1.77 | 2.582(2) | 172 | -1/2+*x*,1/2-*y*,1/2+*z* |
| O10-H10…O19 | 0.82 | 1.85 | 2.652(2) | 168 | 5/2-*x*,-1/2+*y*,1/2-*z* |
| O11-H11…O10 (intra) | 0.82 | 2.26 | 2.698(2) | 114 |  |
| O11-H11…O8 | 0.82 | 2.14 | 2.805(2) | 138 | 1/2+*x*,1/2-*y*,-1/2+*z* |
| O12-H12…O11 (intra) | 0.82 | 2.41 | 2.724(2) | 103 |  |
| O12-H12…O8 | 0.82 | 2.18 | 2.967(2) | 160 | -1/2+*x*,1/2-*y*,-1/2+*z* |
| N18-H18…O8 | 0.86 | 2.15 | 2.961(2) | 156 | 1/2+*x*,1/2-*y*,-1/2+*z* |
| C17–H17…O12 | 0.93 | 2.68 | 3.606(2) | 172 |  |
| **GA-3HP molecular salt** | | | | | |
| **D-H...A** | **D-H** | **H...A** | **D...A** | **D-H...A** | **Symmetry Code** |
| O10-H10…O11 (intra) | 0.82 | 2.28 | 2.715(2) | 114 |  |
| O10-H10…O19 | 0.82 | 2.38 | 3.012(2) | 135 | 1/2-*x*,1/2+*y*,3/2-*z* |
| O11-H11…O12 (intra) | 0.82 | 2.37 | 2.727(2) | 108 |  |
| O11-H11…O8 | 0.82 | 1.90 | 2.703(2) | 165 | 3/2-*x*,1/2+*y*,3/2-*z* |
| O12-H12…O9 | 0.82 | 1.85 | 2.655(2) | 169 | 1/2+*x*,1/2-*y*,1/2+*z* |
| N18-H18…O9 | 0.98 | 1.67 | 2.642(2) | 179 | 1-*x*,-*y*,1-*z* |
| O19-H19…O8 | 0.82 | 1.75 | 2.566(2) | 172 | -1/2+*x*,1/2-*y*,1/2+*z* |
| C7-H7…O9 | 0.93 | 2.55 | 3.204(2) | 128 | 1/2+*x*,1/2-*y*,1/2+*z* |
| **GA-4HP cocrystal hydrate** | | | | | |
| **D-H...A** | **D-H** | **H...A** | **D...A** | **D-H...A** | **Symmetry Code** |
| O9-H9…O8 | 0.98 | 1.64 | 2.620(2) | 178 | 1-*x*,2-*y*,-*z* |
| O10-H10…O19 | 0.82 | 1.86 | 2.652(3) | 163 | -*x*,1-*y*,-*z* |
| O11-H11…O20 | 0.82 | 1.85 | 2.668(3) | 174 | -1+*x*,1/2-*y*,-1/2+*z* |
| O12-H12…O11 (intra) | 0.82 | 2.28 | 2.720(2) | 114 |  |
| O12-H12…O11 | 0.82 | 2.11 | 2.827(2) | 145 | -*x*,-*y*,-*z* |
| N18-H18…O20 | 0.92 | 2.08 | 2.882(3) | 145 |  |
| N18-H18…O10 | 0.92 | 2.37 | 2.979(3) | 123 | 1+*x*,1/2-*y*,1/2+*z* |
| O20-H20A…O19 | 0.85 | 1.91 | 2.744(3) | 165 | 1-*x*,1/2+*y*,1/2-*z* |
| O20-H20B…O19 | 0.85 | 1.86 | 2.706(3) | 176 | 1+*x*,*y*,*z* |
| C14-H14…O12 | 0.93 | 2.56 | 3.469(3) | 166 |  |
| C17-H17…O8 | 0.93 | 2.29 | 3.053(3) | 139 | 1-*x*,-1/2+*y*,1/2-*z* |

**Table S3**. Comparison of experimental (XRD) and theoritical (DFT) parameters of intermolecular interactions responsible for the formation of multicomponent compounds.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **Bond lenghts (Å)** | | | | | | **Bond angles (°)** | | **Torsion angles (°)** | |
| **XRD** | **DFT** | **XRD** | **DFT** | **XRD** | **DFT** | **XRD** | **DFT** | **XRD** | **DFT** |
| **GA-2HP** | C17-H17…O12 | | C17-H17 | | H17…O12 | | C17-H17…O12 | | N18-C17-H17…O12 | |
| 3.606 | 3.927 | 0.93 | 1.082 | 2.682 | 3.914 | 172.65 | 82.73 | 146.22 | 6.24 |
|  | | | | | | | | C16-C17-H17…O12 | |
| -33.75 | -173.82 |
| **GA-4HP** | C14-H14…O12 | | C14-H14 | | H14…O12 | | C14-H14…O12 | | C15-C14-H14…O12 | |
| 3.469 | 3.468 | 0.93 | 0.93 | 2.558 | 2.559 | 166.05 | 166.06 | -76.01 | -76.11 |
|  | | | | | | | | C13-C14-H14…O12 | |
| 103.93 | 103.83 |
| N18-H18…O20 | | N18-H18 | | H18…O20 | | N18-H18…O20 | | C13-N18-H18…O20 | |
| 2.882 | 2.882 | 0.917 | 0.917 | 2.080 | 2.079 | 145.36 | 145.41 | 104.10 | 103.79 |
|  | | | | | | | | C17-N18-H18…O20 | |
| -74.03 | -74.34 |
| **GA-3HP** | π-π interactions | | **Cg(1)-Cg(2) distance in Å** | | | | | | | |
| **XRD** | | | | **DFT** | | | |
| 3.828 | | | | 3.574 | | | |

**Table S4.** Lone pair…π interactions in GA-2HP (Å, ).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Y-X...Cg(π) | X...Cg | Y-X...Cg | Y-X...Cg | Symmetry code |
| C15-H15...Cg(1) | 2.97 | 3.731(2) | 140 | 2*-x,*1*- y,*1*-z* |
| C13-O19...Cg(1) | 3.439(18) | 3.512(2) | 82.68(12) | 3/2*-x,*1/2*+y,* 1/2*-z* |

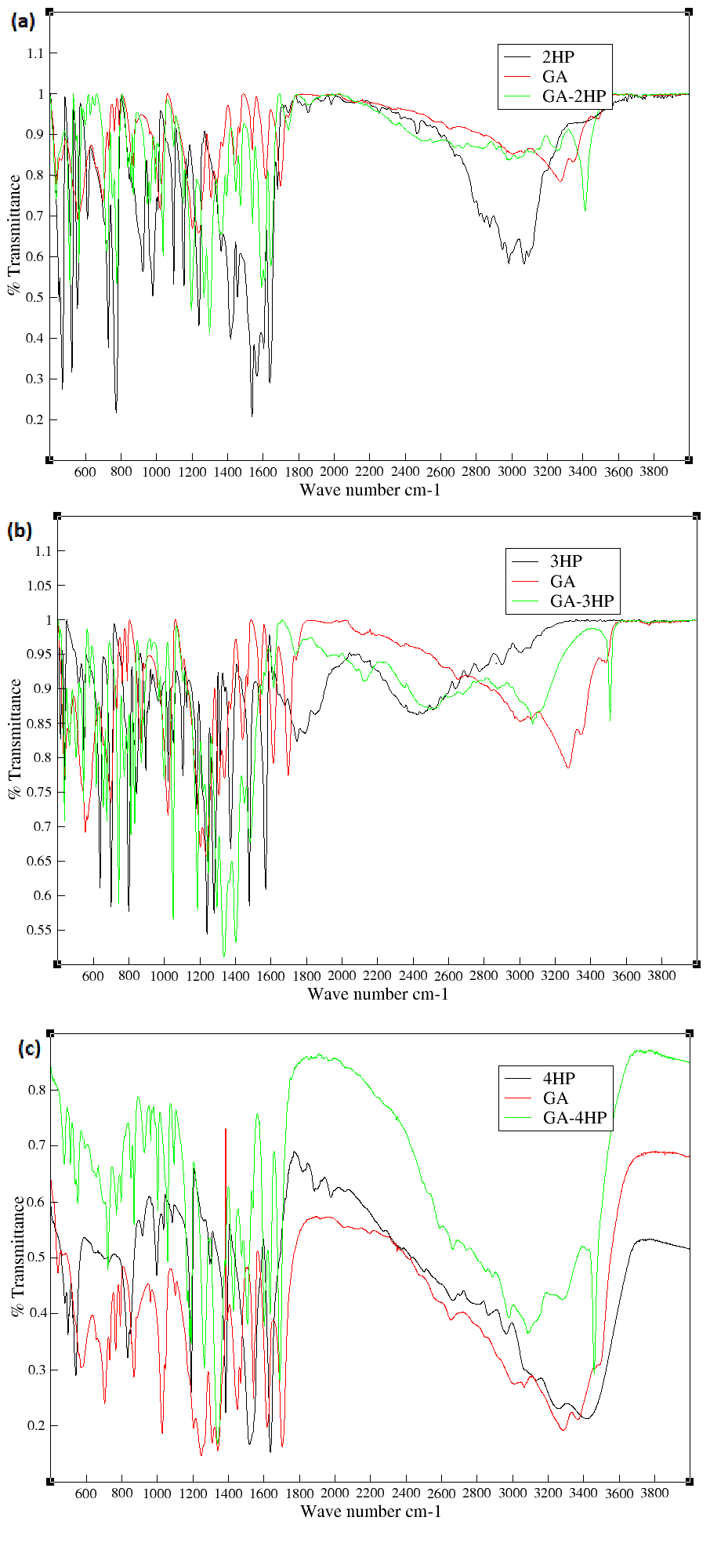
**Table S5.** π-π interactions.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Cg(I) - Cg(J)** | **Cg...Cg in Å** |  |  |  | **CgI-Perp** | **CgJ-Perp** | **Symmetry code** |
| GA-2HP cocrystal | | | | | | | |
| Cg(1) - Cg(1) | 5.5486(14) | 0 | 56.9 | 56.9 | 3.0333(8) | -3.0332(8) | -1+*x*, *y*, *z* |
| Cg(1) - Cg(2) | 5.8335(13) | 75.16(10) | 44.8 | 62.5 | 2.6916(8) | 4.1369(9) | *x*, *y*, *z* |
| Cg(1) - Cg(2) | 4.0924(12) | 3.09(10) | 36.3 | 34.3 | 3.3792(8) | -3.2840(9) | 3/2-*x*, -1/2+*y*, 1/2-*z* |
| Cg(1) - Cg(2) | 4.9509(13) | 75.16(10) | 13.8 | 82.5 | 0.6472(8) | 4.8088(9) | 2-*x*, 1-*y*, 1-*z* |
| Cg(2) - Cg(2) | 5.5486(14) | 0 | 58.4 | 58.4 | 2.9037(9) | -2.9037(9) | -1+*x*,*y*,*z* |
| Cg(2) - Cg(2) | 4.1012(13) | 0 | 35.5 | 35.5 | 3.3389(9) | -3.3388(9) |  |
| GA-3HP molecular salt | | | | | | | |
| Cg(1) - Cg(1) | 5.7181(12) | 69 | 54.3 | 38.6 | 4.4694(8) | -3.3375(8) | 3/2-*x*,-1/2+*y*,3/2-*z* |
| Cg(1) - Cg(1) | 4.5004(11) | 0 | 41.5 | 41.5 | 3.3682(8) | 3.3682(8) | 1-*x*,1-*y*,1-*z* |
| Cg(1) - Cg(2) | 3.8277(13) | 6.97(10) | 18.2 | 11.6 | 3.7493(8) | -3.6352(9) | *x*,*y*,*z* |
| Cg(1) - Cg(2) | 5.8022(14) | 75.58(10) | 44.0 | 80.9 | 0.9132(8) | 4.1752(9) | 3/2-*x*,1/2+y,3/2-*z* |
| Cg(2) - Cg(2) | 4.0034(13) | 0 | 26.2 | 26.2 | -3.5915(9) | -3.5914(9) | 1-x, -y, 2-z |
| GA-4HP cocrystal hydrate | | | | | | | |
| Cg(1) - Cg(1) | 3.5070(14) | 0 | 13.9 | 13.9 | -3.4042(10) | -3.4042(10) | -*x*,1-*y*,-*z* |
| Cg(1) - Cg(1) | 5.5399(14) | 0 | 57.0 | 57.0 | 3.0142(10) | 3.0142(10) | 1-*x*,1-*y*,-*z* |
| Cg(2) - Cg(2) | 3.6360(18) | 2 | 8.0 | 10.2 | -3.5780(12) | 3.6005(12) | 1-*x*,1/2+*y*,1/2-*z* |

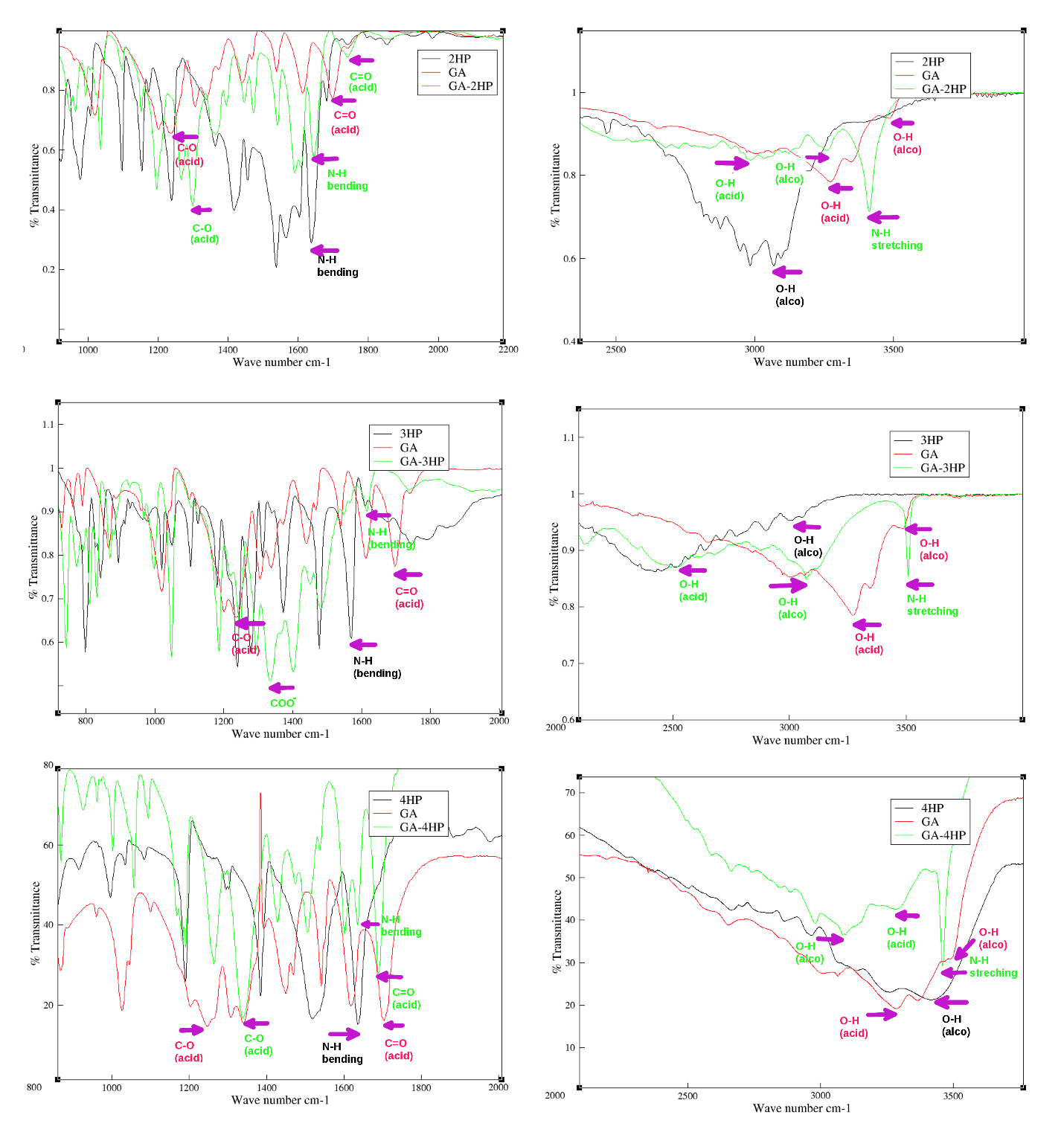
Where, α is the dihedral angle between planes I and J, β is the angle between the Cg(I)→Cg(J) vector and the normal to the plane I, γ is the angle between the Cg(I)→Cg(J) vector and the normal to the plane J, CgI-Perp is the perpendicular distance of CgI from ring J and CgJ-Perp is the perpendicular distance of CgJ from ring I.

**Table S6.** Summary of the percentage contribution of various intermolecular contacts to the Hirshfeld surface.

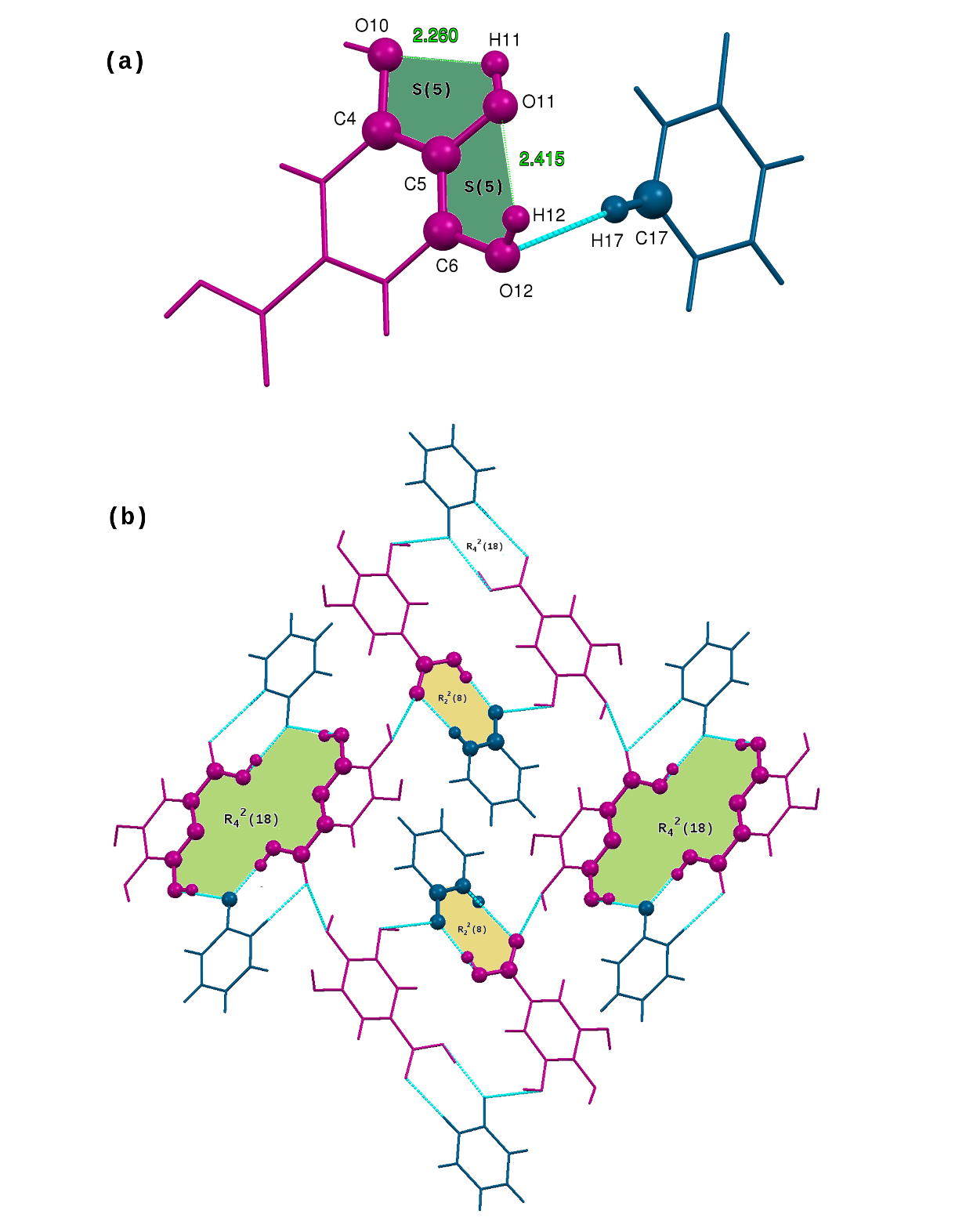
|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **O…H** | **H…H** | **C…H** | **C…C** | **O…C** | **C…N** | **O…O** | **N…H** | **N…N** |
| GA-2HP | 37.1 | 29.2 | 18.1 | 4.1 | 6.5 | 0.5 | 2.3 | 1.5 | 0.0 |
| GA-3HP | 46.2 | 33.7 | 10.5 | 3.3 | 3.9 | 0.1 | 1.1 | 1.0 | 0.0 |
| GA-4HP | 41.9 | 31.3 | 12.3 | 7.3 | 3.3 | 2.3 | 1.4 | 0.1 | 0.0 |



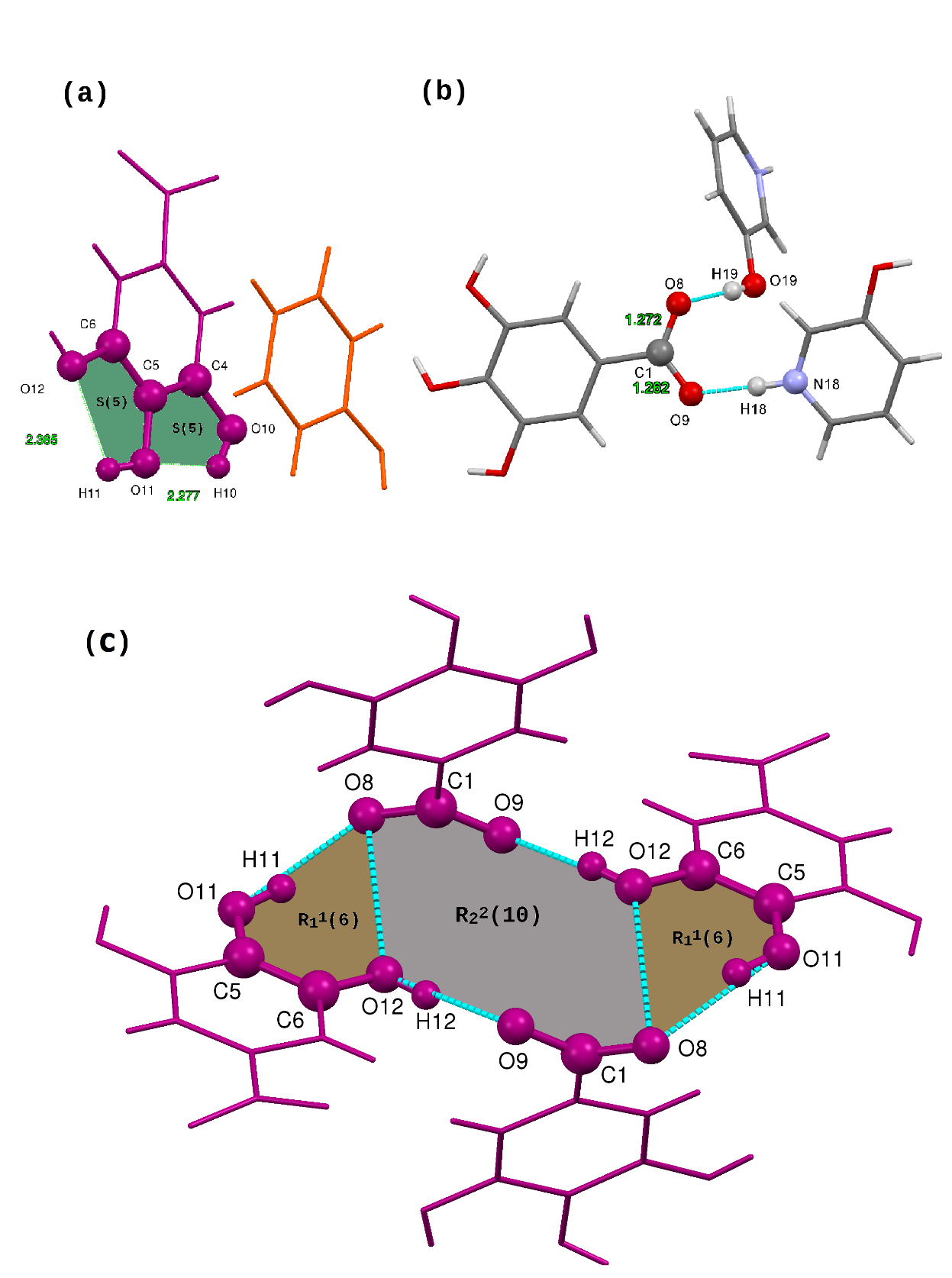
**Figure S1:** FTIR spectrum of starting components and ground materials of (a) GA-2HP cocrystal, (b) GA-3HP molecular salt and (c) GA-4HP monohydrate cocrystal.

****

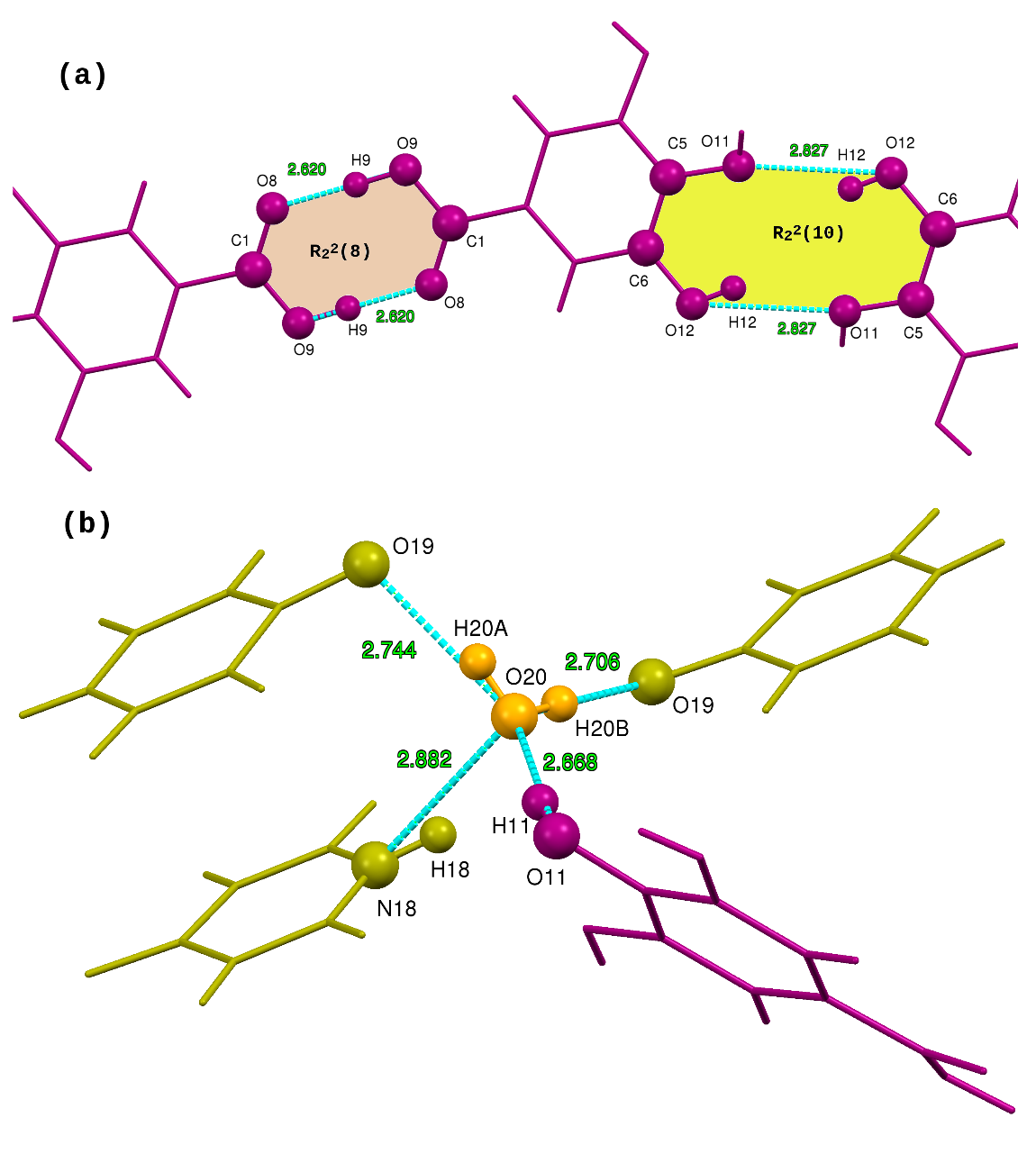
**Figure S2:** IR frequency assignment of the functional groups.



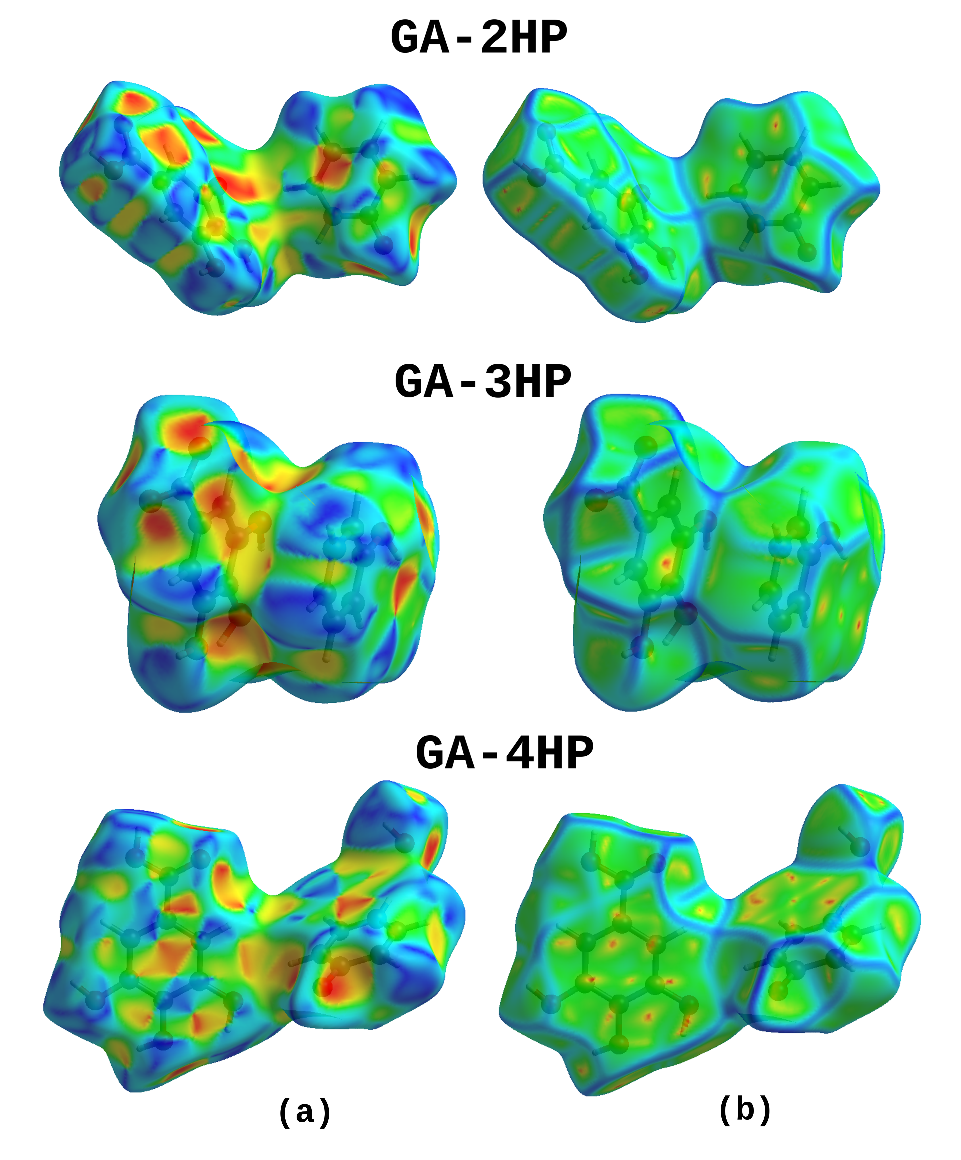
**Figure S3:** (a) Assymetric unit of 1:1GA-2HP molecular salt showing *S*(5) patterns and (b) the presence of and ring motifs.



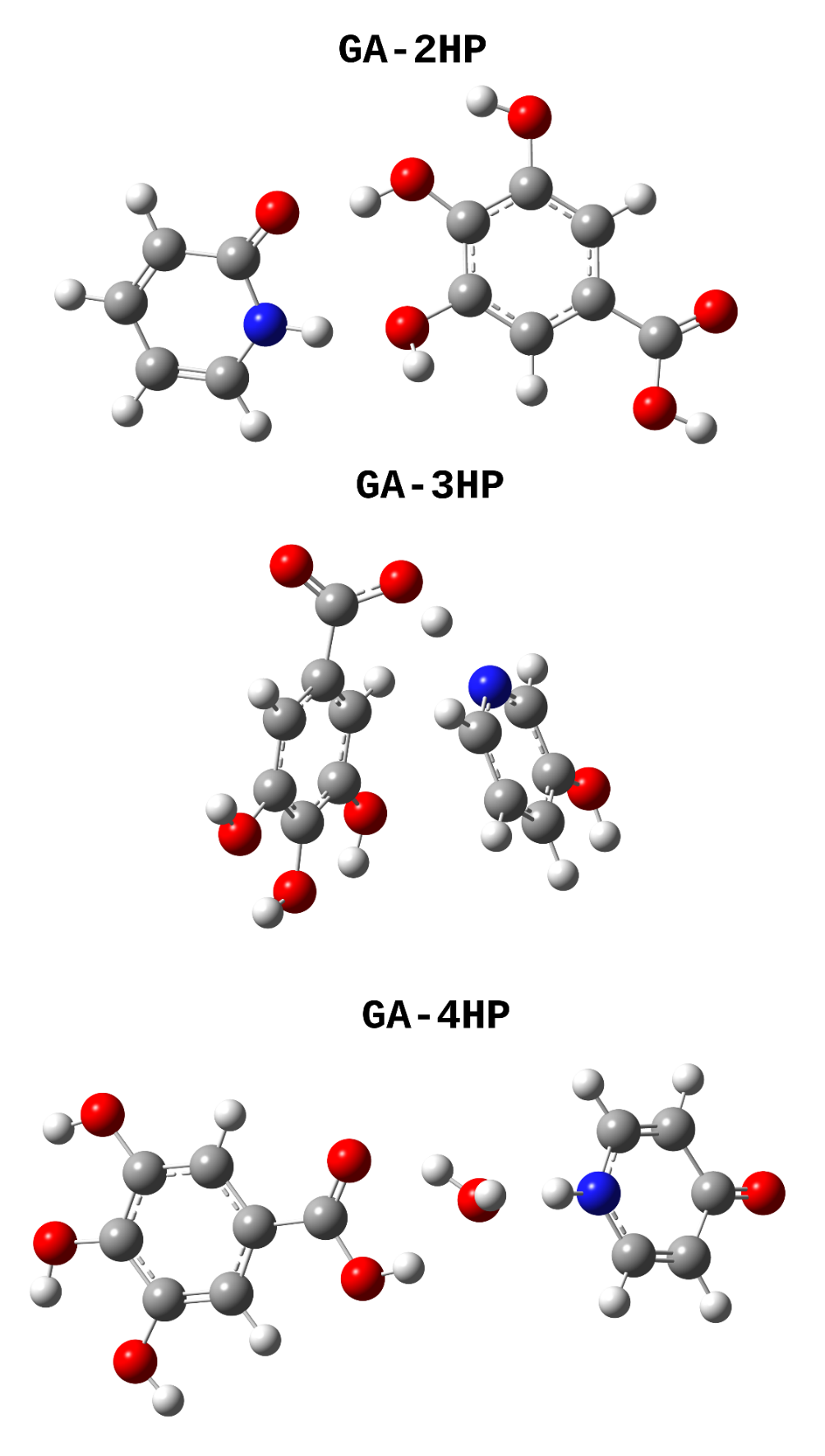
**Figure.S4:** (a) Assymetric unit of 1:1 GA-3HP molecular salt showing *S*(5) patterns, (b) highlighting the C-O bond lengths confirming the proton transfer from GA to 3HP and (c) the presence of and ring motifs.



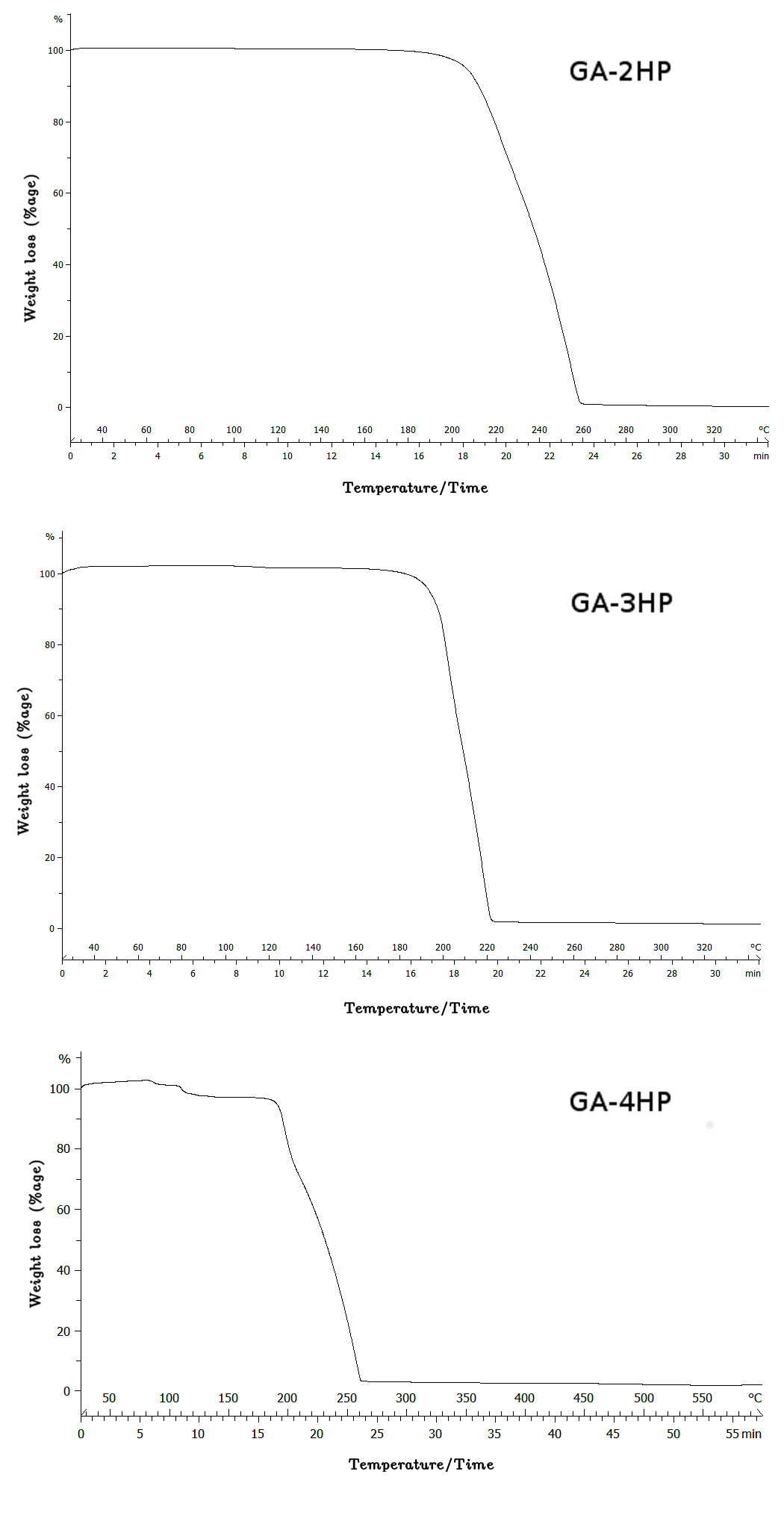
**Figure S5:** (a) The presence of and ring motifs in GA-4HP cocrystal monohydrate and (b) strong hydrogen bond DDAA environment of the water molecule.



**Figure S6:** Views of the Hirshfeld surfaces mapped with shape index and curvedness of the three reported multicomponent crystals.



**Figure S7:** DFT optimized structures of (a) GA-2HP cocrystal, (b) GA-3HP molecular salt and (c) GA-4HP monohydrate cocrystal.



**Figure S8:** TGA thermograms of (a) 1:1 GA-2HP shows that the cocrystal melts at 210C and decomposes at 260C, (b) 1:1 GA-3HP shows that the molecular salt melts at 195C and decomposes at 220C and (c) 1:1 GA-4HP monohydrate cocrystal shows a weight loss of 6.36% at 100C which indicates the removal of one molecule of water, it melts at 190C and decomposes at 260C.