

## Exploring the hydrogen bonding features and electron localisation of molecules of bisglycine with HX ( X = Br, Cl, I, F) using quantum chemical computations, AIM and ELF analysis along with vibrational spectral studies

Sarah Susan Jolly<sup>a</sup>, Twinkle A R<sup>\*a</sup>, Arunsasi B S<sup>b</sup> & Reshma R<sup>c</sup>

<sup>a</sup>Department of Physics, Mar Ivanios College, Thiruvananthapuram 695 015, India

<sup>b</sup>Kerala Fire and Rescue Services, Pulimoodu Thiruvananthapuram 605 001, India

<sup>c</sup>Mar Baselios College of Engineering and Technology, Thiruvananthapuram 695 015, India

E-mail: [twinkle.ar@mic.ac.in](mailto:twinkle.ar@mic.ac.in)

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In this work we have focused our attention entirely on the bonding features of compounds of bisglycine with all the hydrohalides, except hydrogen astatide. On the basis of the quantum mechanical calculations in B3LYP/cc-PVTZ levels, the geometric parameters have been calculated along with infrared spectral analysis. Raman spectral analysis and topological analysis have also been carried out. A detailed analysis on the nature of the hydrogen bonding using topological parameters, such as electronic charge density, Laplacian of electronic charge density, kinetic and potential energy density which have been evaluated at bond critical points, have also been presented. In addition to employing several powerful computational methods like NBO, QTAIM and ELF, experimental and theoretical spectral analyses have also been done to substantiate the study.

**Keywords:** Bisglycine Hydrohalides, NBO, QTAIM, ELF

Over the past thirty years scientific world is looking keenly for efficient nonlinear optical materials for their crucial applications in medical field, solar cell, telecommunication, laser technology, optical computation, *etc.*<sup>1,2</sup>. Although many of the amino acids are already reported to have NLO activity, since glycine has no asymmetric carbon atom, it can exist in Zwitterionic form, and is also capable of forming compounds with several types of charged and neutral chemical compounds. The capacity of halogen atom to act as an acceptor of hydrogen bonds is of much interest in a variety of fields<sup>3</sup>. Both halogen ligands as well as halide ions have proved to be hydrogen bond acceptors in numerous cases<sup>4</sup>. The crystal structure of bis glycine hydrogen bromide (BGHB) reported earlier by Sampthkrishnan<sup>5</sup>. Glycine derivatives like glycine sodium nitrate<sup>6</sup>, bis-glycine maleate<sup>7</sup>, bis-glycine lithium nitrate<sup>8</sup>, and glycine nitrate<sup>9</sup> are reported to have good NLO efficiency and are comparable to KDP with a better transparency window.

Although there are some reports on the bonding characteristics of compounds of HBr, HCl, HF, HI, *etc.* with organic acids, a detailed study, both with the help of Density Functional Theory (DFT) level

computational methods and spectral analyses has not been reported so far to the best of our knowledge. In this paper we present an extensive and comprehensive study on bonding features, especially the hydrogen bonding of compounds of four hydrohalides with bis-Glycine, with the help of analyses of Optimized Geometry, Natural Bond Orbital (NBO), Quantum Theory of Atoms in Molecule (QTAIM), Electron Localisation Function (ELF) and FT-IR & FT-Raman Spectra. The first compound, bis-Glycine Hydrogen Bromide (BGHB), was grown by us, while the structural details of the other three crystals, bis-Glycine Hydrogen Chloride (BGHC), bis-Glycine Hydrogen Fluoride (BGHF) and bis-Glycine Hydrogen Iodide, were obtained from previous reports and the data base of Cambridge Crystallographic Data Centre (CCDC). In this study we have concentrated on N-H...X, N-H...O and N-H...N interactions.

### Experimental Section

#### Preparation

The BGHB salt was synthesized by dissolving high purity AR grade glycine and hydrobromic acid in molar ratio of 2:1 in deionised water at room

temperature. The solution is kept undisturbed for few weeks and crystalline BGHB salt was obtained by slow evaporation.

### Characterization

FT-IR spectrum recording of the sample has been carried out in the range  $4000\text{--}400\text{ cm}^{-1}$  by Perkin Elmer spectrometer using the KBr Pellet technique. The FT-Raman spectrum recording was also carried out in the range of  $3500\text{--}50\text{ cm}^{-1}$  using Perkin Elmer GX 2000 FT-Raman spectrometer.

### Computational details

The quantum chemical calculations employed in vibrational spectroscopic studies are of paramount importance in the understanding of fundamental modes of vibrations of the chemical compounds. Optimization of geometrical structure (Fig. 1, Table 1) of the molecule was performed with GAUSSIAN09 (Ref. 10) using different functionals and the B3LYP functional with cc-PVTZ basis set is used for further calculations.

The approach of Quantum Theory of Atoms in molecule (QTAIM) proposed by Bader *et al.*<sup>11,12</sup> has been confirmed to be effective and convenient for identifying the non-covalent interactions and their

interaction energy with only the molecular geometry as input. The bond topological properties such as electron density and Laplacian (Fig. 2, Table 2) of the electron density were determined from the Bader Theory of Atoms in Molecules implemented in AIMALL software<sup>13</sup>. The molecular graph of BGHB showing different bond path has been plotted using Multiwfn<sup>14</sup>. The interaction energy - IHB calculated from the Espinosa hypothesis<sup>15</sup>.

Natural Bond Orbital (Fig. 3, Table 3) calculation has been carried out at the B3LYP /cc-PVTZ level of theory using NBO 3.1 program<sup>16</sup>. NBO analyses provide a coherent method for studying intra and inter molecular bonding interaction among bonds, and also provide a convenient basis for investigation of charge transfer or conjugative interactions in molecular system<sup>17,18</sup>. Another useful aspect of NBO method is that it gives information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra and intermolecular interactions. The computed NBOs are useful in understanding the distribution of electron density on the stability and reactivity of the systems. The NBO analysis offers a way to quantify delocalization energies from second-order orbital interaction and to study hybridization and molecular bonding, despite being a powerful technique for studying hybridization and molecular bonding.

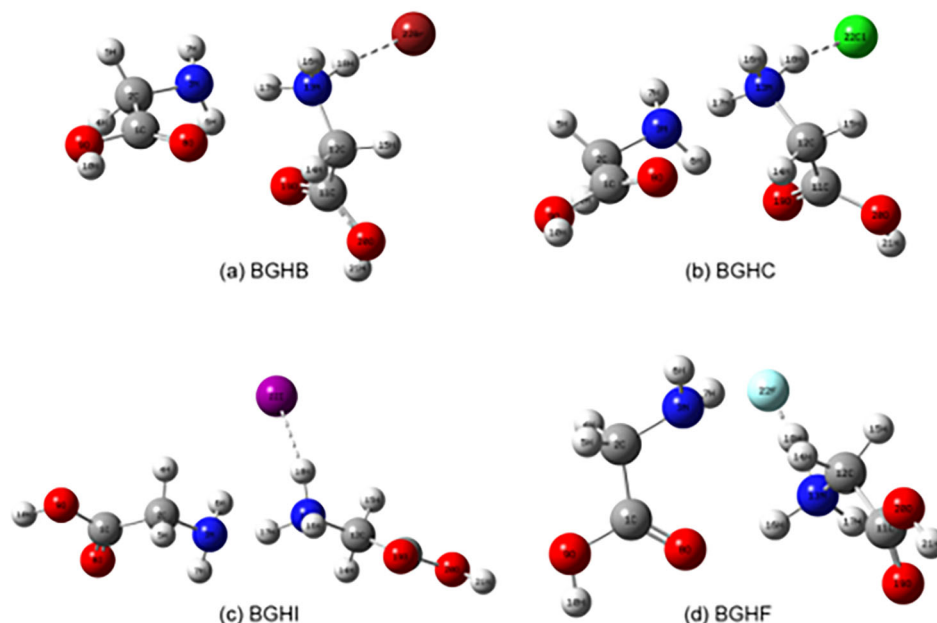


Fig. 1 — Molecular structure of molecules calculated at B3LYP/cc-PVTZ

Table 1 — Optimized geometrical parameters (Å) of BGHX(X=Br/Cl/F/I) atom labeling is according to Fig.1.

Bond Length	Exp.	Calc. BGHB	Calc. BGHC	Calc. BGHF	Calc. BGHI
C <sub>2</sub> -C <sub>1</sub>	1.52	1.51	1.52	1.52	1.52
C <sub>2</sub> -N <sub>3</sub>	1.48	1.45	1.46	1.45	1.48
C <sub>2</sub> -H <sub>4</sub>	0.97	1.09	1.10	1.10	1.09
H <sub>5</sub> -C <sub>2</sub>	0.97	1.09	1.09	1.09	1.09
H <sub>6</sub> -N <sub>3</sub>	0.89	1.01	1.02	1.01	1.03
H <sub>7</sub> -N <sub>3</sub>	0.89	1.01	1.01	1.02	1.02
O <sub>8</sub> -C <sub>1</sub>	1.24	1.20	1.24	1.24	1.23
O <sub>9</sub> -C <sub>1</sub>	1.25	1.34	1.38	1.38	1.37
H <sub>10</sub> -O <sub>9</sub>	0.81	0.96	0.98	0.98	0.98
C <sub>11</sub> -C <sub>12</sub>	1.49	1.51	1.52	1.51	1.51
C <sub>12</sub> -N <sub>13</sub>	1.47	1.47	1.49	1.48	1.46
H <sub>14</sub> -C <sub>12</sub>	0.96	1.08	1.09	1.09	1.09
H <sub>15</sub> -C <sub>12</sub>	0.97	1.08	1.09	1.09	1.09
H <sub>16</sub> -C <sub>13</sub>	0.90	1.01	1.02	1.03	1.02
H <sub>17</sub> -C <sub>13</sub>	0.88	1.04	1.06	1.02	1.11
H <sub>18</sub> -C <sub>13</sub>	0.90	1.11	1.12	1.35	1.07
O <sub>19</sub> -C <sub>11</sub>	1.20	1.20	1.24	1.23	1.24
O <sub>20</sub> -C <sub>11</sub>	1.31	1.33	1.37	1.38	1.37
H <sub>21</sub> -O <sub>20</sub>	0.82	0.96	0.98	0.98	0.98
X <sub>22</sub> ...H <sub>18</sub>	1.80	1.93	1.80	1.09	2.36
N <sub>13</sub> ...X <sub>22</sub>	2.62	3.03	2.89	2.43	3.32
N <sub>3</sub> ...X <sub>22</sub>	5.01	4.85	4.43	2.81	3.64

Calc.: Calculated, Exp.: Experimental. X=Br/Cl/F/I

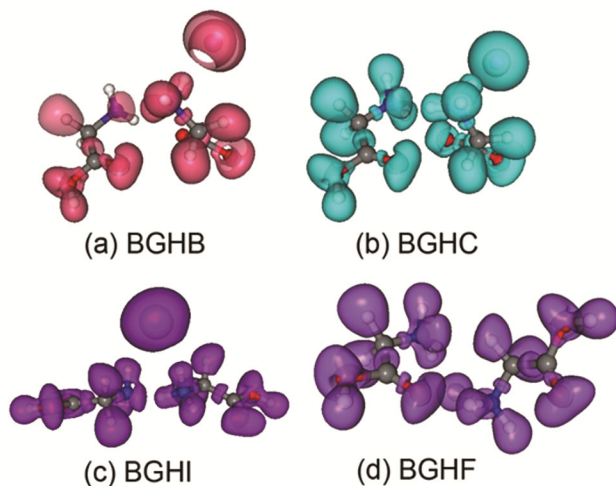


Fig. 2 — Molecular graph of molecules of different bond path at critical points at (3,-1)

The topological analysis of ELF (Fig. 4, Table 4) provides a detailed insight into the electronic structure in molecules, offering an atom based partition of the molecular space where electrons get maximum localized. The electron localization function was analyzed with the TopMod<sup>19</sup> program using density matrices obtained from Gaussian orbital computations. ELF provides a convenient characterization of hydrogen bond, due to the

Table 2 — Topological parameters for bonds of interacting atoms, electron density  $\rho(r)$  and Laplacian of electron density  $\nabla^2\rho(r)$ 

Molecule	Bond	$\rho(r)$	$\nabla^2\rho(r)$
BGHB	N <sub>13</sub> - H <sub>18</sub> ...Br <sub>22</sub>	0.33	0.24
	N <sub>3</sub> - H <sub>6</sub> ...O <sub>19</sub>	0.07	1.20
	N <sub>13</sub> - H <sub>17</sub> ...N <sub>3</sub>	0.20	1.45
BGHC	N <sub>13</sub> - H <sub>18</sub> ...Cl <sub>22</sub>	0.40	2.40
	N <sub>3</sub> - H <sub>6</sub> ...O <sub>19</sub>	0.14	2.17
	N <sub>13</sub> - H <sub>17</sub> ...N <sub>3</sub>	0.27	2.65
BGHF	N <sub>13</sub> - H <sub>18</sub> ...F <sub>22</sub>	0.80	0.72
	N <sub>3</sub> - H <sub>7</sub> ...F <sub>22</sub>	0.20	2.89
	N <sub>13</sub> - H <sub>16</sub> ...O <sub>8</sub>	0.15	0.24
BGHI	N <sub>13</sub> - H <sub>18</sub> ...I <sub>22</sub>	0.20	0.96
	N <sub>3</sub> - H <sub>6</sub> ...I <sub>22</sub>	0.80	0.72
	N <sub>13</sub> - H <sub>16</sub> ...O <sub>19</sub>	0.07	1.93
	N <sub>13</sub> - H <sub>17</sub> ...N <sub>3</sub>	0.47	2.89

presence of a protonated valence basin sharing a separatrix with at least another valence basin which does not participate to same atomic valence shell<sup>20</sup>. The protonated valence basin is generally a disynaptic, whereas the valence basin is monosynaptic (involving lone pair), disynaptic (H-bond involving a bond) or protonated disynaptic.

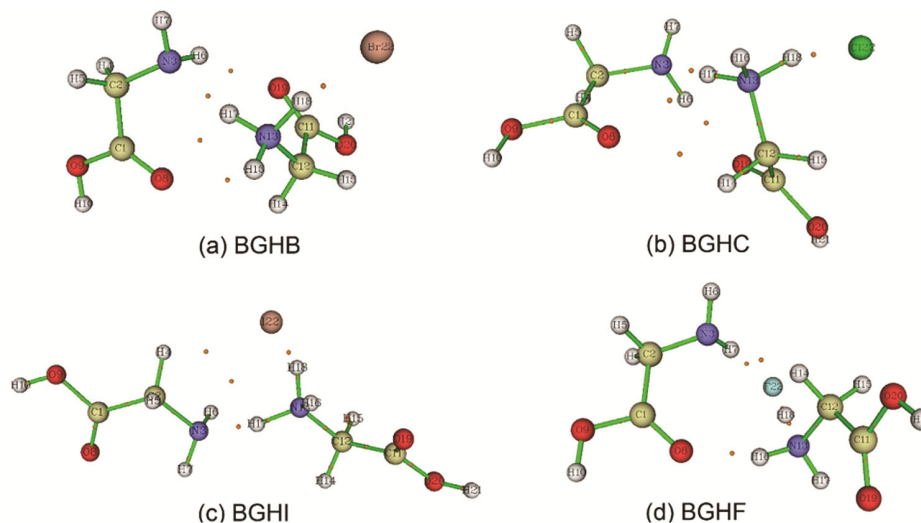
Fig. 3 — Electron Localization Function value defining the bonding isosurface  $\eta(r) = 0.82$  for the molecules

Table 3 — Second order perturbation theory analysis of Fock matrix in NBO basis of the Molecules

Donor (i)	ED (i)	Acceptor (j)	ED (j)	E(2) (kcal mol <sup>-1</sup> )
(a) BGHB				
n(2)O <sub>8</sub>	1.8499	$\sigma^* \text{C}_1\text{-C}_2$	0.0835	21.58
n(2)O <sub>8</sub>	1.8499	$\pi^* \text{C}_1\text{-O}_9$	0.0933	31.50
n(2)O <sub>9</sub>	1.8203	$\pi^* \text{C}_1\text{-O}_8$	0.2169	48.80
n(1)N <sub>3</sub>	1.9143	$\sigma^* \text{N}_{13}\text{-H}_{17}$	0.0558	16.52
n(4)Br <sub>22</sub>	1.7746	$\sigma^* \text{N}_{13}\text{-H}_{18}$	0.2156	72.96
n(2)O <sub>20</sub>	1.8122	$\pi^* \text{C}_{11}\text{-O}_{19}$	0.2194	50.47
n(1)Br <sub>22</sub>	1.7746	$\sigma^* \text{N}_{13}\text{-H}_{18}$	0.2156	5.83
(b) BGHC				
Donor (i)	ED (i)	Acceptor (j)	ED (j)	E(2) (kcal mol <sup>-1</sup> )
n(2)O <sub>8</sub>	1.8624	$\sigma^* \text{C}_1\text{-C}_2$	0.0689	16.25
n(2)O <sub>8</sub>	1.8624	$\pi^* \text{C}_1\text{-O}_9$	0.0982	31.25
n(2)O <sub>9</sub>	1.8237	$\pi^* \text{C}_1\text{-O}_8$	0.2228	46.18
n(1)N <sub>3</sub>	1.9143	$\sigma^* \text{N}_{13}\text{-H}_{17}$	0.0558	16.52
n(4)Cl <sub>22</sub>	1.7611	$\sigma^* \text{N}_{13}\text{-H}_{18}$	0.2189	75.55
n(2)O <sub>20</sub>	1.8084	$\pi^* \text{C}_{11}\text{-O}_{19}$	0.2448	48.12
n(1)Cl <sub>22</sub>	1.9991	$\sigma^* \text{N}_{13}\text{-H}_{18}$	0.2189	4.07
(c) BGHF				
Donor (i)	ED (i)	Acceptor (j)	ED (j)	E(2) (kcal mol <sup>-1</sup> )
n(2)O <sub>8</sub>	1.8633	$\sigma^* \text{C}_1\text{-C}_2$	0.0715	14.08
n(2)O <sub>8</sub>	1.8633	$\pi^* \text{C}_1\text{-O}_9$	0.0968	31.69
n(2)O <sub>9</sub>	1.8254	$\pi^* \text{C}_1\text{-O}_8$	0.2254	45.78
n(1)N <sub>3</sub>	1.9396	$\sigma^* \text{C}_1\text{-C}_2$	0.0715	5.32
n(1)O <sub>8</sub>	1.9626	$\sigma^* \text{N}_{13}\text{-H}_{16}$	0.0332	7.34
n(2)O <sub>8</sub>	1.8633	$\sigma^* \text{N}_{13}\text{-H}_{16}$	0.0332	4.73
n(3)F <sub>22</sub>	1.9596	$\sigma^* \text{N}_3\text{-H}_7$	0.0392	15.4
n(1)N <sub>3</sub>	1.9396	$\sigma^* \text{C}_2\text{-H}_4$	0.0309	8.19
n(1)O <sub>8</sub>	1.9626	$\sigma^* \text{C}_1\text{-C}_2$	0.0715	3.80
n(2)O <sub>8</sub>	1.8633	$\sigma^* \text{C}_1\text{-O}_9$	0.0968	31.69
n(2)O <sub>8</sub>	1.8633	$\sigma^* \text{N}_{13}\text{-H}_{16}$	0.0332	4.71
n(1)N <sub>13</sub>	1.9626	$\sigma^* \text{H}_{18}\text{-F}_{22}$	0.2114	124.96

(Contd.)

Table 3 — Second order perturbation theory analysis of Fock matrix in NBO basis of the Molecules (*Contd.*)

Donor (i)	ED (i)	(d) BGHI Acceptor (j)	ED (j)	E(2) (kcal mol <sup>-1</sup> )
n(2)O <sub>8</sub>	1.8587	$\sigma^* C_1-C_2$	0.0694	16.73
n(2)O <sub>8</sub>	1.8587	$\pi^* C_1-O_9$	0.0989	31.61
n(2)O <sub>9</sub>	1.8228	$\pi^* C_1-O_8$	0.2200	46.40
n(1)N <sub>3</sub>	1.8370	$\sigma^* C_1-C_2$	0.0694	5.99
n(1)N <sub>3</sub>	1.8370	$\sigma^* N_{13}-H_{17}$	0.1362	57.20
n(3)I <sub>22</sub>	1.9654	$\sigma^* N_3-H_6$	0.0306	4.02
n(1)I <sub>22</sub>	1.9995	$\sigma^* N_{13}-H_{18}$	0.1280	1.26
n(4)I <sub>22</sub>	1.8461	$\sigma^* N_{13}-H_{18}$	0.1280	26.81

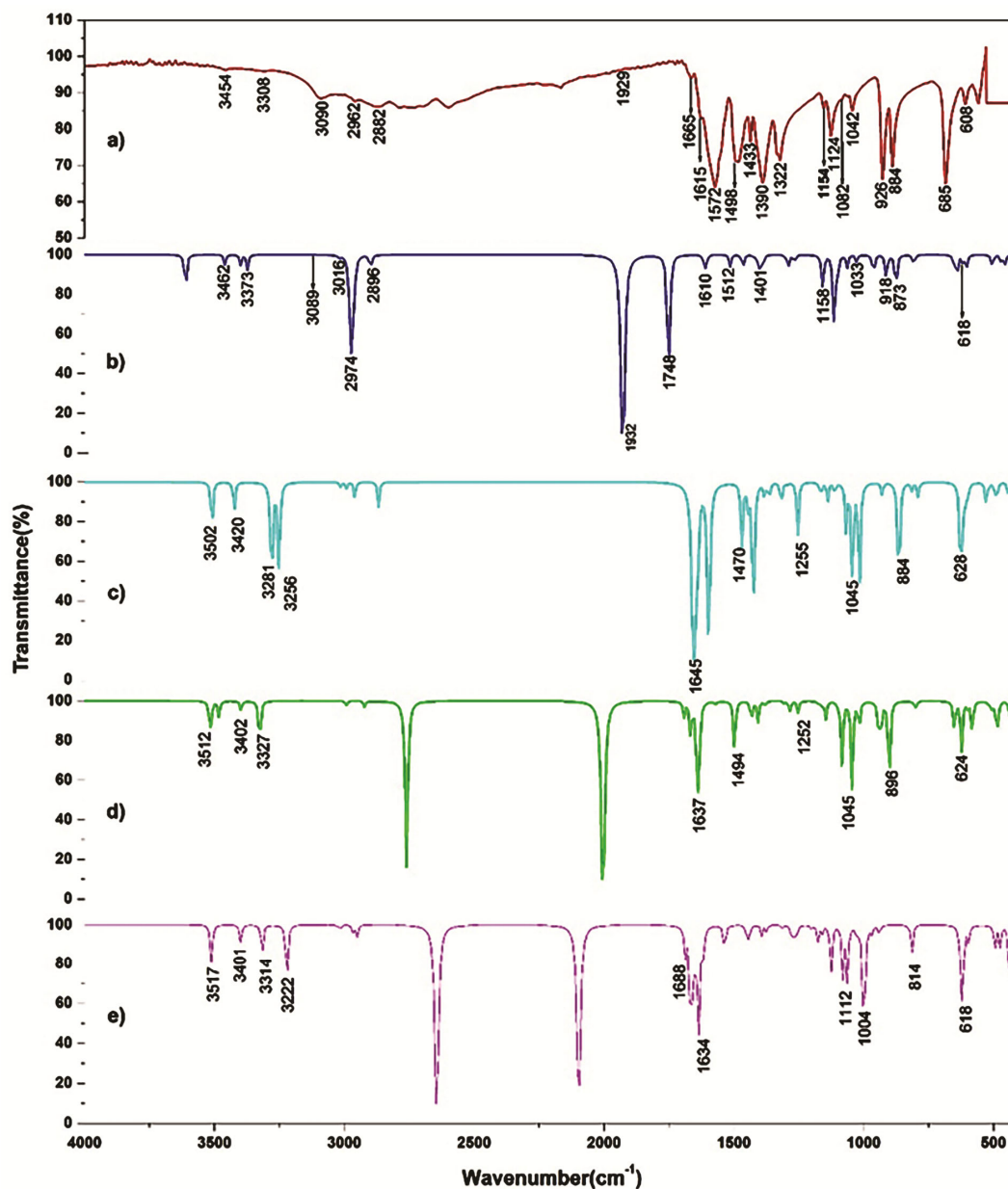


Fig. 4 — Experimental and simulated FT-IR spectra of the molecules in the range 4000–400 cm<sup>-1</sup> (a) BHGB Experimental, (b) BGHB Theoretical, (c) BGHF Theoretical, (d) BGHC Theoretical, (e) BGHI Theoretical

Table 4 — Different types of disynaptic basins, ELF value at attractor (ELF), basins population (N), standard deviation ( $\sigma^2$ ) and relative fluctuation ( $\lambda$ )

(a) BGHB						
BASINS	ELF	N	$\sigma^2$	$\lambda$	Total	
V(N <sub>13</sub> , H <sub>16</sub> )	1.000	2.00	0.77	0.38	1	
V(N <sub>13</sub> , H <sub>17</sub> )	0.999	2.07	0.93	0.41	1	
V(N <sub>13</sub> , H <sub>18</sub> )	0.998	2.13	1.02	0.44	1	
V(N <sub>3</sub> , H <sub>7</sub> )	0.855	2.10	0.94	0.42	1	
V(N <sub>3</sub> , H <sub>6</sub> )	0.764	1.90	0.76	0.41	1	
(b) BGHC						
BASINS	ELF	N	$\sigma^2$	$\lambda$	Total	
V(N <sub>13</sub> , H <sub>16</sub> )	1.000	1.97	0.77	0.39	1	
V(N <sub>13</sub> , H <sub>17</sub> )	0.999	2.17	0.93	0.42	1	
V(N <sub>13</sub> , H <sub>18</sub> )	0.998	2.28	1.02	0.44	1	
V(N <sub>3</sub> , H <sub>7</sub> )	1.000	2.22	0.94	0.42	1	
V(N <sub>3</sub> , H <sub>6</sub> )	1.000	1.88	0.76	0.40	1	
(c) BGHF						
BASINS	ELF	N	$\sigma^2$	$\lambda$	Total	
V(N <sub>13</sub> , H <sub>16</sub> )	1.000	2.09	0.81	0.42	1	
V(N <sub>13</sub> , H <sub>17</sub> )	0.999	1.92	0.93	0.40	1	
V(N <sub>3</sub> , H <sub>7</sub> )	1.000	2.40	0.86	0.42	1	
V(N <sub>3</sub> , H <sub>6</sub> )	1.000	1.80	0.78	0.40	1	
(d) BGHI						
BASINS	ELF	N	$\sigma^2$	$\lambda$	Total	
V(N <sub>13</sub> , H <sub>16</sub> )	1.000	2.00	0.81	0.40	1	
V(N <sub>13</sub> , H <sub>17</sub> )	0.999	2.14	0.93	0.43	1	
V(N <sub>13</sub> , H <sub>18</sub> )	0.998	2.27	1.00	0.44	1	
V(N <sub>3</sub> , H <sub>7</sub> )	1.000	2.05	0.86	0.41	1	
V(N <sub>3</sub> , H <sub>6</sub> )	1.000	1.92	0.78	0.40	1	

## Results and Discussion

### N – H ...X Interaction

The hydrogen bonded interaction between N13 on one side and the halogen atom (X22) on the other side with H18 in between, depends greatly on the relative electronegativities of the N13 and H18 atoms. The spatial distance between N13 and X22 also exhibits a trend supporting this argument. The distances increase in the order 2.43 Å, 2.89 Å, 3.03 Å and 3.32 Å for N...F, N...Cl, N...Br, N...I, respectively. The interaction energy calculated from NBO analysis emphasizes this. In BGHI, the Hydrogen bonding interactions  $n_1(I22) \rightarrow \sigma^*(N13 - H18)$  and  $n_4(I22) \rightarrow \sigma^*(N13 - H18)$  have stabilization energies 1.26 Kcalmol<sup>-1</sup> and 26.81 Kcalmol<sup>-1</sup> respectively. Interaction energy of a comparable order is visible in the case of BGHB, where  $n_1(B22) \rightarrow \sigma^*(N13 - H18)$  and  $n_4(B22) \rightarrow \sigma^*(N13 - H18)$  have energies 5.83 Kcalmol<sup>-1</sup> and 72.96 Kcalmol<sup>-1</sup> respectively. A similar trend is observed in BGHC also. Here we have interaction energies of 4.07 Kcalmol<sup>-1</sup> and 75.55 Kcalmol<sup>-1</sup> for  $n_1(Cl22) \rightarrow \sigma^*(N13 - H18)$  and  $n_4(Cl22) \rightarrow \sigma^*(N13 - H18)$ , respectively. Although

a similar pattern is observed for BGHF molecule, there is an order reversal in charge transfer, which is clearly due the large electronegativity of the fluorine atom. Here the interaction is between the lone pair of N13 and  $\sigma^*(H18 - F22)$ , with a very high interaction energy of 124.96 Kcalmol<sup>-1</sup>. There is also a moderate interaction of the order of 3.90 Kcalmol<sup>-1</sup> between the core electron of N13 and  $\sigma^*(H18 - F22)$ . While examining the system with Quantum theory of atoms in molecule, the total electron density  $\rho(r)$  for the interactions N13 – H18...I22, N3 – H6...I22, N13 – H18...Br22, N13 – H18...Cl22, N13...H18 – F22 and N3 – H7...F22 are 0.20 eÅ<sup>-3</sup>, 0.80 eÅ<sup>-3</sup>, 0.33 eÅ<sup>-3</sup>, 0.40 eÅ<sup>-3</sup> and 0.80 eÅ<sup>-3</sup> and 0.20 eÅ<sup>-3</sup> respectively. The Laplacian of electron density  $\nabla^2\rho(r)$  values for the above-mentioned reactions are 0.96 eÅ<sup>-5</sup>, 0.72 eÅ<sup>-5</sup>, 0.24 eÅ<sup>-5</sup>, 2.40 eÅ<sup>-5</sup>, 0.72 eÅ<sup>-5</sup> and 2.89 eÅ<sup>-5</sup> in the same order. From the above entries, it is clear that all the values for the total electron density  $\rho(r)$  are very low and all the values for Laplacian of electron density  $\nabla^2\rho(r)$  are positive, indicating strong hydrogen bonded interactions. When we carry out the ELF analysis for the BGHC molecule,

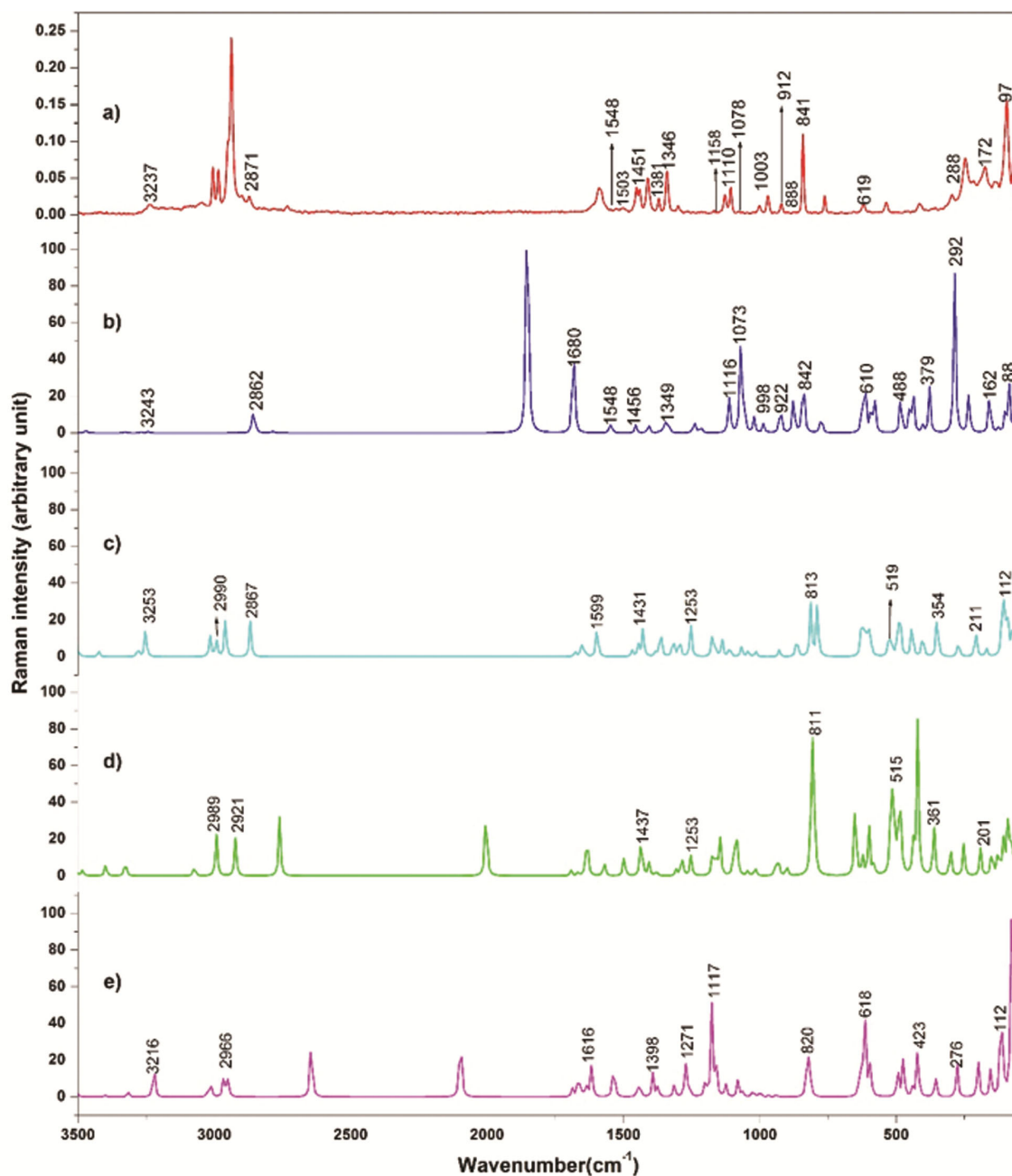


Fig. 5 — Experimental and simulated FT-IR Raman spectra of the molecules in the range 4000–400  $\text{cm}^{-1}$  (a) BHGB Experimental, (b) BGHB Theoretical, (c) BGHF Theoretical, (d) BGHC Theoretical, (e) BGHI Theoretical

the population and relative fluctuation for the basin  $V(N_{13}, H_{18})$  are 2.28 and 0.44 respectively, whereas for the basins  $V(N_{13}, H_{16})$  and  $V(N_{13}, H_{17})$  the corresponding values are 1.97 & 0.39 and 2.17 & 0.42 respectively. The higher values for the basins  $V(N_{13}, H_{16})$  and  $V(N_{13}, H_{17})$  confirm hydrogen bonded interaction. For the molecule BGHB, the corresponding values for the basins  $V(N_{13}, H_{18})$ ,  $V(N_{13}, H_{17})$ ,  $V(N_{13}, H_{16})$  are 2.13 & 0.44, 2.07 & 0.41,

and 2.00 & 0.38 respectively. While looking into the next system -BGHI, the values for the above-mentioned basins are 2.27 and 0.44, 2.14 & 0.43 and 2.00 & 0.40 respectively. In BGHF, as expected, the basin  $V(N_{13}, H_{18})$  is absent whereas the values for the basins  $V(N_{13}, H_{17})$  and  $V(N_{13}, H_{16})$  are 1.92 and 0.40 and 2.09 & 0.42 respectively.

In the spectral analysis of BGHB, the presence of  $H_{18} \dots Br_{22}$  is observed in Raman (Fig. 5, Table 5) at

Table 5 — Assignment of selected fundamental vibrations of the molecules based on scaled quantum mechanical force field calculations

Interaction	BGHB		BGHB		BGHC		BGHF		BGHI	
	Observed		SCALED	PED	SCALED	PED(%)	SCALED	PED(%)	SCALED	PED
	IR (cm <sup>-1</sup> )	RAMAN (cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(%)	(cm <sup>-1</sup> )		(cm <sup>-1</sup> )		(cm <sup>-1</sup> )	(%)
X <sub>22</sub> ...H <sub>18</sub>		306	300	70	363	67	1597	14	278	30
N <sub>13</sub> -H <sub>18</sub>	1932		1921	85	2004	86	611	17		
N <sub>13</sub> -H <sub>17</sub>	2962	2952	2964	67	2761	99	3425	91	2098	69
N <sub>13</sub> -H <sub>16</sub>		3554	3523	99	3534	92	3382	86	3450	62
N <sub>3</sub> -H <sub>6</sub>		3368	3360	76					3222	77
H <sub>6</sub> ...O <sub>19</sub>		3237	3295	76	3301	52				
H <sub>16</sub> ...O <sub>18</sub>							3382	15		

306 cm<sup>-1</sup> and is calculated at 300 cm<sup>-1</sup> with 70% contribution as obtained from the calculation of Potential Energy Distribution (PED)<sup>21</sup>. For N<sub>13</sub> – H<sub>18</sub> interaction, a peak is observed in IR at 1932 cm<sup>-1</sup>, where for N<sub>13</sub> – H<sub>16</sub> and N<sub>13</sub> – H<sub>17</sub> these bands are observed in IR spectrum at 3368 cm<sup>-1</sup> and 2962 cm<sup>-1</sup> respectively<sup>22</sup>. For N<sub>13</sub> – H<sub>17</sub> a weak band is also observed in Raman spectrum at 2952 cm<sup>-1</sup>. The corresponding theoretical values for the above three interactions are 1921 cm<sup>-1</sup>, 3523 cm<sup>-1</sup> and 3084 cm<sup>-1</sup> respectively. From these values, it is also clear that H<sub>18</sub> has a strong interaction with Br<sub>22</sub> and H<sub>17</sub> has a weak interaction with N<sub>3</sub>, whereas H<sub>16</sub> has no interaction at all. For BGHC, H<sub>18</sub>...Cl<sub>22</sub> interaction is calculated at 363 cm<sup>-1</sup>. Here also, for N<sub>13</sub> – H<sub>18</sub>, N<sub>13</sub> – H<sub>17</sub> and N<sub>13</sub> – H<sub>16</sub>, all the counterpart interactions show the similar trend whose theoretical values are given by 2004 cm<sup>-1</sup>, 2761 cm<sup>-1</sup> and 3534 cm<sup>-1</sup> with PED contributions of 86%, 99% and 92% respectively. For BGHI, while the corresponding value for first of the above four interactions is calculated at 278 cm<sup>-1</sup>, the second interaction is absent and this is evident from the structure of the molecule. The values for the third and fourth interactions are 3450 cm<sup>-1</sup> and 2098 cm<sup>-1</sup> respectively. For BGHF, the range for the first interaction is slightly different from the mentioned range for all the other three molecules and is observed at 1724 cm<sup>-1</sup>. This is due to the strong pull of H<sub>18</sub> towards the F<sub>22</sub> atom. This was also evident from the NBO calculations. The interactions of N<sub>13</sub> with H<sub>16</sub> and H<sub>17</sub> are calculated at 3382 cm<sup>-1</sup> and 3425 cm<sup>-1</sup> respectively.

#### N – H ...O Interaction

The NBO analysis gives evidence for the interaction between N – H of one unit and the oxygen

of the carboxyl group belonging to the other unit. In BGHC and BHGB, the O<sub>19</sub> atom acts as the donor and the N<sub>3</sub> – H<sub>6</sub> bond acts as acceptor, while in the case of BGHF, the charge transfer is from the first unit to the second unit. But we experience no such interaction for BGHI molecule. In BGHC, n<sub>1</sub>(O<sub>19</sub>) → σ\*(N<sub>3</sub> – H<sub>6</sub>) interaction has an energy of 4.00 Kcalmol<sup>-1</sup> and n<sub>2</sub>(O<sub>19</sub>) → σ\*(N<sub>3</sub> – H<sub>6</sub>) interaction the stabilization energy is 3.90 Kcalmol<sup>-1</sup>. But the interaction is a little bit less in the case of BGHB. In BGHB, the stabilization energies for above mentioned two interactions are 0.80 Kcalmol<sup>-1</sup> and 0.95 Kcalmol<sup>-1</sup> respectively. The difference in strengths of hydrogen bonds is also obvious from the optimized geometry. In BGHC the O<sub>19</sub>...H<sub>6</sub> distance is 1.99 Å whereas in BGHB the corresponding distance is 2.19 Å. The low interaction energy between O<sub>19</sub> and N<sub>3</sub> – H<sub>6</sub> is also attributed to the partial double bond character of C<sub>11</sub> – O<sub>20</sub> bond. The C<sub>11</sub> – O<sub>20</sub> bond length for BGHB is about 1.33 Å, which is the least among the four molecules under study. As we move on to the discussion of BGHF, the charge transfer is from unit 1 to unit 2, as already mentioned. The n<sub>1</sub>(O<sub>8</sub>) → σ\*(N<sub>13</sub> – H<sub>16</sub>) interaction energy is 7.34 Kcalmol<sup>-1</sup> and n<sub>2</sub>(O<sub>8</sub>) → σ\*(N<sub>13</sub> – H<sub>16</sub>) interaction stabilizes at an energy of 4.73 Kcalmol<sup>-1</sup>. The optimized O<sub>8</sub>...H<sub>16</sub> distance is 1.88 Å. Now we will substantiate our idea for N – H...O interactions of these four molecules with the help of Quantum theory of atoms in molecules. For BGHB and BGHC the interactions are between N<sub>3</sub> – H<sub>6</sub>...O<sub>19</sub> whereas for BGHI and BGHF the interactions are between / among N<sub>13</sub> – H<sub>16</sub>...O<sub>19</sub> and N<sub>13</sub> – H<sub>16</sub>...O<sub>8</sub>. The total electron density values ρ(r) for these interactions are 0.07 eÅ<sup>-3</sup> for BGHI, 0.07 eÅ<sup>-3</sup> for BGHB, 0.14 eÅ<sup>-3</sup> for BGHC and 0.15 eÅ<sup>-3</sup> for BGHF. In the same order, the values for

Laplacian of electron density  $\nabla^2\rho(r)$  are  $1.93 \text{ e}\text{\AA}^{-5}$ ,  $1.20 \text{ e}\text{\AA}^{-5}$ ,  $2.17 \text{ e}\text{\AA}^{-5}$ ,  $0.24 \text{ e}\text{\AA}^{-5}$ . Here also we see, very low total electron density values  $\rho(r)$  and positive Laplacian of electron density values  $\nabla^2\rho(r)$ , confirming that the nature of interactions is hydrogen bonding. When we carry out the ELF analysis for this interaction for the BGHC molecule, the population and relative fluctuation for the basins  $V(N_3, H_6)$  and  $V(N_3, H_7)$  are 1.88 and 0.40 and 2.22 & 0.42 respectively where as for the BGHB molecule, the corresponding values are 1.90 and 0.41 and 2.10 & 0.42 respectively. For BGHI these interactions have a value 1.92 & 0.40 and 2.05 & 0.41 and the corresponding values for the BGHF molecule are found to be 1.80 & 0.40 and 2.40 & 0.42 respectively. Here also the higher values of the basins confirm the hydrogen bonded interactions.

Again, for the spectral analysis part of this interaction, for BGHB molecule,  $H6...O19$  is observed as a strong band in Raman at  $3237 \text{ cm}^{-1}$  and the calculated value is observed at  $3295 \text{ cm}^{-1}$  with 76% PED contribution. For BGHC molecule also, there is a similar interaction with almost the same wave number. For BGHF the interaction is  $N13 - H16...O18$ , ie the interaction is between  $H16$  and  $O18$  and is observed at  $3382 \text{ cm}^{-1}$ . Here the PED is only 15% and therefore this band is not clearly visible in experimental spectra. As discussed above no such interaction is evident for BGHI molecule.

### N – H ...N Interaction

In our study we find that there are intramolecular hydrogen bonded interactions for all the molecules except BGHF. For BGHI the  $n_1(N3) \rightarrow \sigma^*(N13 - H17)$  interaction energy is  $57.20 \text{ Kcalmol}^{-1}$ . In case of BGHB and BGHC, energy values for  $n_1(N3) \rightarrow \sigma^*(N13 - H17)$  are  $16.52 \text{ Kcalmol}^{-1}$  and  $27.01 \text{ Kcalmol}^{-1}$  respectively. The absence of this  $N13 - H17...N3$  interaction in BGHF is due to the strong pull of both  $N3$  and  $N13$  towards the fluorine atom. These interactions together have an energy of  $140.36 \text{ Kcalmol}^{-1}$  which is very large compared to other interactions. Optimized geometry also gives a clue in this regard that the  $N3 - X22 - N13$  bond angle for BGHF is  $81.89^\circ$ , which is much greater than their other counterparts. The interatomic distances also validate the same.  $N3... F22$  distance and  $N13... F22$  distance is almost equal indicating that the fluorine atom occupies a

symmetric position between two units. The hydrogen bonded interactions become clearer when we look into the system using the aid of Quantum theory of atoms in molecules, and as mentioned earlier we can see that the  $N13 - H17...N3$  interactions are present for all molecules except BGHF. Here also, we can see the total electron density values  $\rho(r)$  are very low which are given by  $0.47 \text{ e}\text{\AA}^{-3}$ ,  $0.20 \text{ e}\text{\AA}^{-3}$  and  $0.27 \text{ e}\text{\AA}^{-3}$  for BGHI, BGHB and BGHC respectively. The Laplacian of electron density values  $\nabla^2\rho(r)$  are all positive given by  $2.89 \text{ e}\text{\AA}^{-5}$ ,  $1.45 \text{ e}\text{\AA}^{-5}$  and  $2.65 \text{ e}\text{\AA}^{-5}$  in the same order. When we carry out the ELF analysis for different molecules, as expected the basin  $V(N13, H17)$  is absent in BGHF. In the molecule BGHC the population and relative fluctuation for the basin  $V(N13, H17)$  are 2.17 & 0.42. For the molecule BGHB the corresponding values are 2.07 & 0.41 respectively. Finally, for BGHI the values for the above mentioned 2.14 & 0.43 respectively.

Now we can go to the spectral analysis part of this interaction. For the BGHB molecule, the interaction between  $H17$  and  $N13$  is observed in Raman at  $2952 \text{ cm}^{-1}$  and in IR at  $2962 \text{ cm}^{-1}$ , while the calculated wave number for this interaction is at  $3084 \text{ cm}^{-1}$  with 67% PED contribution<sup>22</sup>. For the molecule BGHC the above-mentioned interaction is calculated at  $2872 \text{ cm}^{-1}$  with 92% contribution. The same interaction is observed at  $2182 \text{ cm}^{-1}$  with 69% contribution for BGHI molecule. There is no corresponding interaction for BGHF molecule and this fact is also evident from other studies which we have discussed above.

### Conclusion

We made a detailed study of the bonding features of four molecules BGHB, BGHC, BGHI, BGHF with special attention to the behaviour of hydrogen bonds of the three selected interactions  $N - H...X$ ,  $N - H...O$  and  $N - H...N$ . We have done different computational studies by exercising different techniques like NBO, QTAIM, ELF together with experimental and theoretical spectral analysis. We found that all these studies are complementary and support each other. In addition to shedding light on the bonding features of several interactions of different hydrohalides of bisglycine, the present study also validates suitability, specificity and accuracy of the different computational methods mentioned here.

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#### Funding

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#### Conflict of Interest

The authors declare that there is no conflict of interest among the authors.

#### Ethical approval

Not applicable.

#### Informed consent

Not applicable.

#### Author contribution

Twinkle A R: Conceptualization, Final Draft and Validation, Reshma R: Writing - Original Draft, Sarah Susan Jolly: Formal Analysis: Arun Sasi B S, Methodology.

#### Data Availability Statement

Experimental and Computational Data sets generated during the current study are available from the corresponding author on reasonable request,

#### Conflicts of interest

There are no conflicts of interest to declare

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