Est. 1984

Density Functional Theory, Natural Bond Orbital and Atoms in Molecule Analyses on the Hydrogen Bonding Interactions in 2-chloroaniline-Carboxylic Acids

M. CHANDRA SEKHAR[1]*, A.VENKATESULU[2], T. MADHU MOHAN[3] and M. GOWRISANKAR[4]

[1]Department of Physics, Vignan Institute of Technology and Science, Deshmukhi, Telagana, India
[2]Department of Physics, Govt. First Grade College, Hosakote, Bangalore Rural, Karnataka, India
[3] Department of Physics, Vasireddy Venkatadri Institute of Technology, Nambur, Andhra Pradesh, India
[4]Department of Chemistry, J.K.C.C. Acharya Nagarjuna University, Guntur-522510, AP, India.
*Corresponding author E-mail: sekharchandra6@gmail.com

ABSTRACT

The DFT method was used to study the hydrogen bonding interactions of 1:1 complexes which are formed between 2-chloroaniline with carboxylic acids at basis set of 6-311++G (d, p) with their optimized geometries, interaction energies, topological features of the electron density and vibrational frequencies. Thirteen 2-chloroaniline – carboxylic acid complexes were found on the potential energy surface involving N-H…N, H-O…H, N-H—O, O-H…N hydrogen bonds. The strength of the hydrogen bond between 2-chloroaniline – carboxylic acid complexes has been explored by calculation of stabilization energy (E(2)) between proton acceptor and proton donor under NBO analysis. The atoms in molecule (AIM) method is an excellent tool to find linear correlation that exist between the hydrogen bond length, electron density ($\rho(r)$) and its Laplacian ($\nabla^2\rho(r)$)) at the bond critical points.

Key words: Carboxylic acids, hydrogen bond, AIM, NBO

INTRODUCTION

The investigations of specific interactions, particularly hydrogen bond, are one of the most frequently studied aspects not only for their diverse molecular topologies, but also for their potential applications in varied ûelds such as chemistry, biology, physics, and so on [1–9]. In this study nature of hydrogen bonding interactions in various molecular systems explained theoretically and experimentally [10-12]. The formation of typical moderate or strong conventional hydrogen bonds is relatively easy to verify, because the presence of these bonds substantially modiûes the structural, energetic and spectroscopic properties of the system.

In the present study of interactions between the compounds plays a very important role in industrially. 2-chloroaniline is used in Agricultural, Pharmaceutical, Rubber chemicals and as a parent substance in the production of antioxidants. It is also used in the manufacturing of synthetic dyes and organic pigments especially for red color. Carboxylic acids are used in ink, pesticides, cosmetics, plastics, and rubber as a chemical constituent. They are also important in industrial applications of compounds with carboxyl groups in the use of fatty acids in making soaps, detergents, and shampoos [13-17].

The main objective of this study is to reveal the nature intermolecular interactions between –NH$_2$ group of 2-chloroaniline and –COOH group of carboxylic acids. The investigation on interaction between 2-chloroaniline and carboxylic acid molecules may provide useful information concerning the bond strength and bond characteristics of compounds that are of fundamental importance for the radical chemistry and the synthesis of organic materials.

In the present study the optimized geometries, interaction energies and vibrational frequencies of this system were calculated by using DFT method. AIM analysis based on Barder's atoms in the molecular theory [18] and NBO analyses are carried out to conform the presence of the hydrogen bonding between the complexes.

Computational details

Geometrical optimization, determination of interaction energy and natural bonding orbital (NBO) analysis have been carried out using density functional theory (DFT) with the popular hybrid method (B3LYP) [18-22]. As polarity of molecule has great influence on intermolecular hydrogen bonding, hydrogen bond orbitals requires large space occupation. Thus, diffuse and polarization functions augmented split valence 6-311++G (d, p) basis set is used for better description of geometrical optimization and natural bonding orbital (NBO) analysis. All these calculations are performed using Gaussian 09[23].

These calculations were performed on self- and cross-associational dimers of 2-chloroaniline with carboxylic acids. For all species analyzed here geometries were optimized and the ûnal complexes correspond to minima since no imaginary frequencies were found. The interaction energies of all dimers were determined from the energy difference between the dimer and monomers in their minimum energy conûguration. The basis set superposition error (BSSE) was eliminated using Boys and Bernard's counterpoise method [24].

Further to evaluate the strength of the intermolecular interactions NBO analyses were performed at B3LYP/6-311++G (d,p) level. AIM theory of Bader was used to analyze the bonding characteristics, which is based on a topological analysis of ρ and $\nabla^2\rho$ by means of Multiwfn program .Finally, thermodynamic data and expected changes upon dimerizing were derived using statistical thermodynamics in the gas phase based on the frequencies analysis.

RESULTS AND DISCUSSION

Structure and energy analysis

The optimized possible structures of all dimers are successfully obtained at the B3LYP/6-311++G (d, p) level. The hydrogen bond geometrical parameters and molecular graphs of the thirteen obtained associations are presented in Table 1 and Figure 1, respectively.

The molecular graphical analysis shows that different types of hydrogen bonds are formed in the obtained association between the donor(X-H) and acceptor group(Y). The change of the X-H bond length during the process of the formation of hydrogen bond (H-bond) association can reflect the characteristic nature of H-bond. As shown in Table 1, all the values of $\Delta R(X-H)$ of hydrogen bonds are positive these values indicate that they are all red shifting hydrogen bonds. Furthermore a hydrogen bond parameter $\Delta R(H-Y)$[25], is defined as $\Delta R (H…Y) =R (H)_{vwr}+ R(Y)_{vwr} \% R(H….Y)$ Where $R(Y)_{vwr}$ and $R(H)_{vwr}$ are the Vander Waals radii of H and Y acceptor atoms obtained by Bondi [26] respectively, $R(X…Y)$ is the distance of hydrogen-donor and hydrogen-acceptor.

The can be estimated the strength of the hydrogen bond. From Table 1 the largest value of is

0.82954 A^0 of the intermolecular OH…..N hydrogen bond in the cross-association **5** which represents the strongest hydrogen bond. The strength of the hydrogen bond in the self associations are presented in the order **3**(O4-H12…O1)> **2**(O2-H4…O3)> **4**(O2-H1….O3)> **1**(N2-H10…N1) and in the cross associations are in order **5**(O2-H10….N1)> **8**(O2-H6….N1)> **11**(O2-H5….N1)> **9**(N1-H14…O1)> **6**(N1-H12…O1)> **12**(N1-H14…O1)> **7**(N1-H12…O2)> **10**(N1-H12…O2)> **13**(N1-H12…O2).

Interaction energy () for the hydrogen-bonded complex is calculated as the difference between the energy of hydrogen bonded complex and the summation of the energies of the each component monomers as given below

$$\Delta E^{cp} = E_{AB}\left(AB\right) - \left[E_A\left(AB\right) + E_B\left(AB\right)\right] \quad ...(1)$$

Where E$_{AB}$(AB) optimized energy of hydrogen is bonded complex, E$_A$(AB) and E$_B$(AB)

Table 1: Structural parameters (bond lengths in A^0) and angles (^{0}) of the hydrogen bonds for all hydrogen bond associations at B3LYP/6-311++G (d, p).

Associations	X-H….Y	R(X-H)	ΔR (X-H)	R(H…..Y)	ΔR(H…Y)	R(X…Y)	∠(XHY)
1	N2-H10…N1	1.01416	0.00611	2.26065	0.48935	3.24571	168.458
2	O2-H4…O3	0.99819	0.03358	1.68401	1.03599	2.68207	179.821
3	O4-H12…O1	0.99874	0.03394	1.67744	1.04256	2.67626	178.973
4	O2-H1….O3	0.99753	0.03271	1.68855	1.03145	2.68597	178.999
5	O2-H10….N1	0.98042	0.01581	1.92046	0.82954	2.89545	168.189
6	N1-H12…O1	1.01369	0.00564	2.10553	0.61447	3.06806	163.189
7	N1-H12…O2	1.01062	0.00257	2.21537	0.50463	3.11535	147.493
8	O2-H6….N1	0.98034	0.01554	1.95335	0.79665	2.90540	161.678
9	N1-H14…O1	1.01306	0.00501	2.09070	0.62930	3.08105	165.205
10	N1-H12…O2	1.01018	0.00213	2.27367	0.44633	3.24805	161.640
11	O2-H5….N1	0.98782	0.02300	1.95837	0.79163	2.90573	168.633
12	N1-H14…O1	1.01229	0.00424	2.14089	0.57911	3.09884	157.163
13	N1-H12…O2	1.01055	0.00250	2.32537	0.39463	3.29767	161.090

Table 2: Interaction energy corrected with BSSE (ΔE.kcal.mol^{-1})for all dimers at B3LYP/6-311++G (d,p) level

Complexes	D-H…..A	ΔE	BSSE	ΔE^{cp}
1	N2-H10…N1	-13.59473	1.10	-12.4947
2	O2-H11…O1	-15.6583	0.84	-14.8183
3	O2-H11…O1	-15.8073	0.85	-14.9573
4	O1-H11…O1	-16.6858	0.88	-15.8058
5	O2-H10….N1	-59.2973	1.68	-57.6173
6	N1-H12…O1	-57.1757	1.61	-55.5657
7	N1-H12…O2	-56.0541	1.63	-54.4241
8	O2-H6….N1	-52.1121	0.96	-51.1521
9	N1-H14…O1	-55.673	1.01	-54.663
10	N1-H12…O2	-52.5054	1.41	-51.0954
11	O2-H5….N1	-52.3241	2.10	-50.2241
12	N1-H14…O1	-54.7146	2.41	-52.3046
13	N1-H12…O2	-50.8679	2.75	-48.1179

is the energies of the individual component monomers, respectively. Interaction energies are corrected for the basis set superposition error

(BSSE) by virtue of counterpoise method [24]. Hydrogen bonded complex is more stable if interaction energy is more negative compared to

Table.3: Topological Properties (in a.u.) of the BCPs of intermolecular H-bonds in 2-chloroaniline and carboxylic acids complexes obtained from the B3LYP/6-311++G (d, p) level calculations

Associations	X-H....Y	ρ	$\nabla^2 r$	V	K	H
1	N2-H10…N1	0.019	0.069	-0.013281	0.015301	0.00202
2	O2-H11…O1	0.04654	0.16176	-0.041903	0.041172	-0.00073
3	O2-H11…O1	0.04702	0.13478	-0.042945	0.038319	-0.00462
4	O1-H11…O1	0.04612	0.1599	-0.041502	0.040739	-0.04150
5	O2-H10….N1	0.03389	0.096901	-0.025285	0.024128	-0.00115
6	N1-H12…O1	0.01858	0.06561	-0.015472	0.015937	0.00046
7	N1-H12…O2	0.01431	0.05449	-0.011967	0.012794	0.00082
8	O2-H6….N1	0.03263	0.08963	-0.026104	0.024256	-0.00184
9	N1-H14…O1	0.0185	0.06696	-0.015394	0.016067	0.00067
10	N1-H12…O2	0.0129	0.04772	-0.010548	0.011239	0.00069
11	O2-H5….N1	0.03178	0.09188	-0.026894	0.025560	-0.00133
12	N1-H14…O1	0.01605	0.05982	-0.013337	0.014146	0.00080
13	N1-H12…O2	0.01106	0.04092	-0.008688	0.009460	0.00077

Table 4: Second-perturbation energies (E(2) / kJ·mol^{-1}) of hydrogen bonds for all hydrogen bond associations obtained by NBO analysis at the B3LYP/6-311++G (d, p) level

Association	Donor NBO(i)	Acceptor NBO(j)	E(2)
1	LP(1) N1	BD*(1)N2-H10	19.83
2	LP(1)O3	BD*(1) O2-H4	13.61
	LP(2)O3	BD*(1) O2-H4	15.55
3	LP (1) O1	BD*(1)O4-H12	8.00
	LP (2) O1	BD*(1)O4-H12	20.63
4	LP (1) O2	BD*(1)O17-H18	8.13
	LP (2) O2	BD*(1)O17-H18	19.02
5	LP(1) N11	BD*(1) O21-H22	15.64
6	LP (1)O1	BD*(1) N1-H12	1.67
	LP (2)O1	BD*(1) N1-H12	3.36
7	LP(1) O2	BD*(1) N1-H12	1.96
8	LP (1) N1	BD*(1) H6-O2	13.56
9	LP(1) O1	BD*(1) N1-H14	2.24
	LP(2) O1	BD*(1) N1-H14	3.05
10	LP(1) O2	BD*(1) N1-H12	1.48
	LP(2) O2	BD*(1) N1-H12	0.41
11	LP(1) N1	BD*(1) O2-H5	13.26
12	LP(1) O1	BD*(1) N1-H14	1.87
	LP(2) O1	BD* (1)N1-H14	0.74
13	LP(1) O1	BD*(1) N1-H14	1.37
	LP(2) O1	BD*(1) N1-H14	0.12

other hydrogen bonded complexes.

The counterpoise-corrected interaction energies, for all the dimers were computed at DFT, B3LYP with basis set 6-311++G (d, p). All the corrected interaction energies are summarized in Table 2 [27.] The trends in interaction energy are similar to the results of geometrical structures. In the cross-association hydrogen bonded complexes the interaction energy is strong in the dimer **5** with O-H….N hydrogen bond of interaction energy -57.6173, KJ.mol^{-1} which is higher than remaining all other cross-associated dimers.

Therefore, in the cross-associations O-H…N hydrogen bonds are stronger than N-H…O hydrogen bond in o-toluidine and isomeric butanol mixtures. This can be explained qualitatively by the fact that the free electron pair around the N atoms with less *s* and more *p* character has a higher polarizability and acts as a good proton acceptor for the donor –OH groups of the alcohols, which are more efficient than the –OH group itself.

Electron density analysis

The existences of the hydrogen bond in all dimers are provided by topological analysis of the electron. So AIM theory elaborated was also applied here to deepen the nature of the intermolecular hydrogen bond of all dimers. The Bader theory is regarded as one of the most efficient tools for investigating electronic character in chemical bond. In the topological theory of AIM, when two neighboring atoms are chemically bonded, a bond critical point appears between them and the nature of chemical bonds and molecular reactivity are described by total electronic density, $\nabla^2\rho(r)$ and its corresponding Laplacian, and the electronic energy density (H), which is composed of the electronic kinetic energy density (G) and the electronic potential energy density (V). The values of AIM topological parameters of the intermolecular hydrogen bond for all dimers are shown in Table 3.

In the present study, the values of $\rho(r)$ and $\nabla^2\rho(r)$ varies from 0.011 to 0.047 a.u and 0.040 to 0.161 a.u. Maximum electron density in the self-association is (0.04702 a.u) and in cross-association is (0.03389 a.u) shows strong

hydrogen bonds are observed for O-H….N interaction with high stability.

The positive values of Laplacian charge density in Table 3 for all molecules at BCPs are positive which reveal that electronic charges are depleted in the interatomic path, which is characteristic of closed shell interactions such as hydrogen bonds. The correlation between hydrogen bond length and electron density are inverse to each other i.e. increase in the hydrogen bond length corresponds to decrease in the electron density. Since there is increase in the distance results in reduced orbital overlap hence electron density decreases along the bond. It is also observed that the Laplacian electron density and hydrogen bond lengths also inversely related. The curves corresponding to correction coefficient for electron density and its Laplacian electron density with hydrogen bond length are shown in the Figure 2. The correlation coefficient of electron density, Laplacian electron density with hydrogen bond distance is observed to be 0.953 and 0.9144.

The total electronic energy density of the charge distribution may be expressed

$$H_{BCP} = K_{BCP} + V_{BCP} \qquad ...(2)$$

For strong hydrogen-bonding interaction, the total electronic energy density *H* is found to be negative (Table 3), showing partially covalent and partially electrostatic in nature, whereas this quantity is positive for medium and weak hydrogen bonds, revealing only electrostatic interactions for this bonding[28].

Natural bond orbital analysis

The natural bonding orbital (NBO) analysis has been a reliable tool for the rationalization of H-bonds that correlate well with changes in bond length in accordance with the basic chemical concepts. It is also used to derive information on the changes of charge densities in proton donor and acceptor as well as in the bonding and antibonding orbitals. For each donor and acceptor, the stabilization energy E (2) associated with hydrogen bonding between sites *i* and *j* are given below,
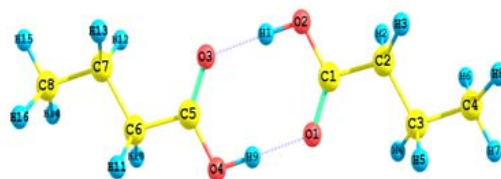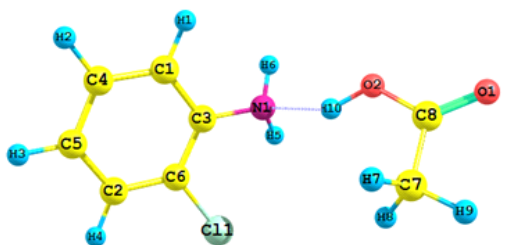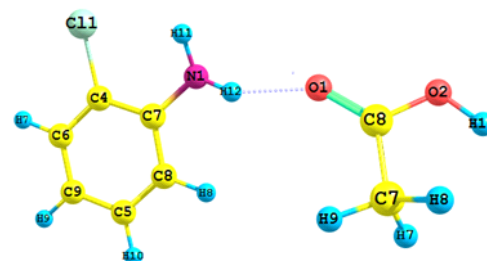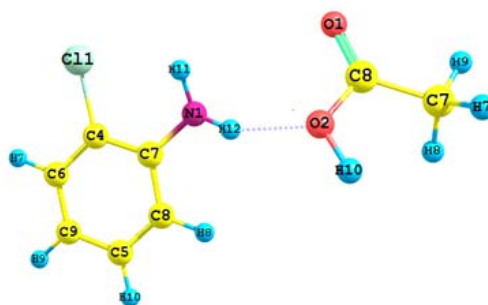
1

2

3

4

5
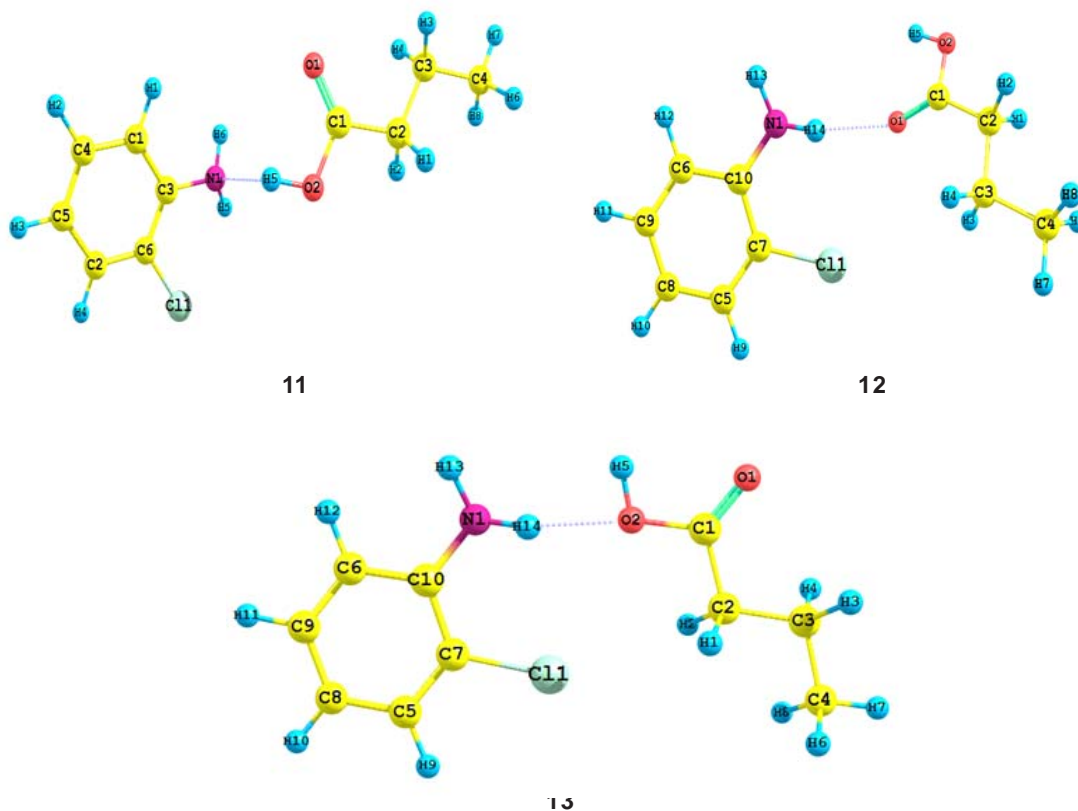

6

7
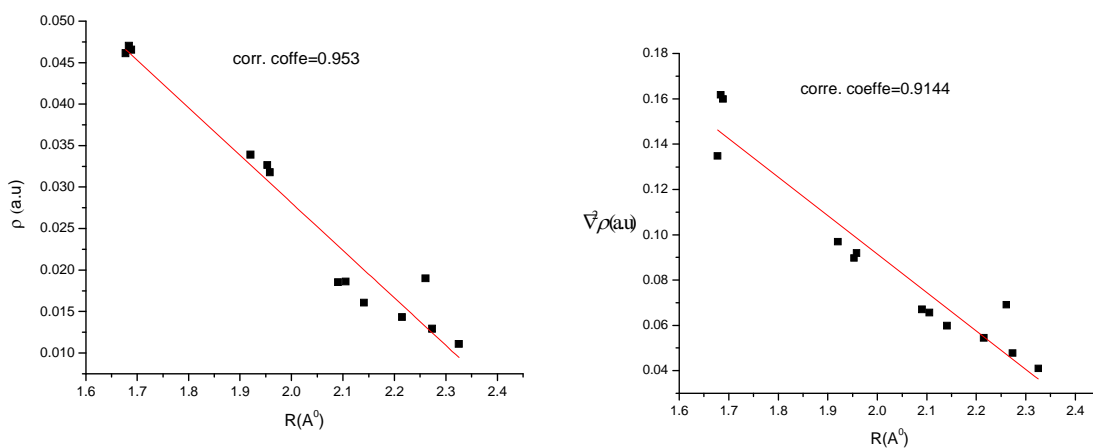


**8**

9

10

11   **12**

13
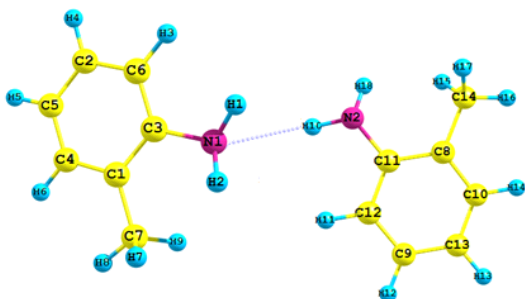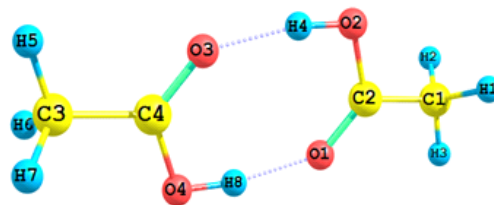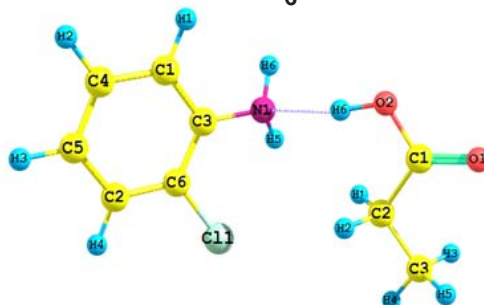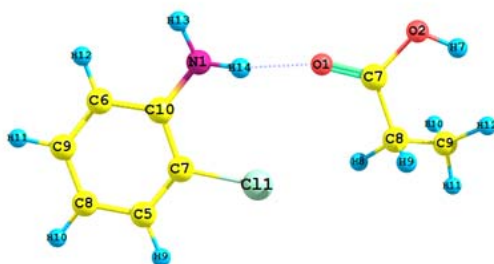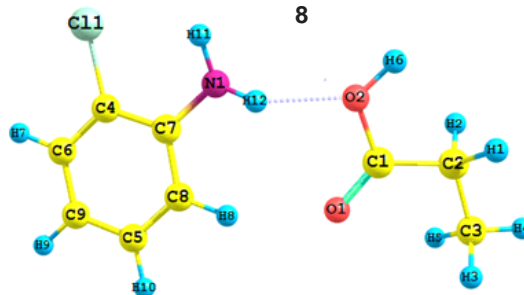
Fig 1: Geometrical optimized structures using 6-311++G (d,p) of self associations 1 (2-Chloroaniline-2-Chloroaniline),2(Ethanoic acid-Ethanoic acid),3(Propanoic acid-propanoic), 4 (Butanoic acid-Butanoic acid) and of cross-associations 5,6,7 (2-Chloroaniline + Ethanoic acid) 8,9,10 (2-Chloroaniline + Propanoic acid),11,12,13 (2-Chloroaniline + Butanoic acid).


Fig 2: The correlation between the electron density and the Laplacian electron density at BCP and hydrogen bond length at B3LYP/6-311++G(d,p) theory for 2-chloroaniline and carboxylic acid complexes
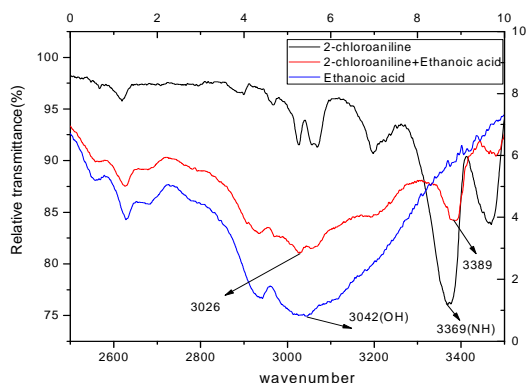
Fig.3. Infrared spectra of pure 2-chloroaniline, pure Ethanoic acid and equimolar binary mixture of 2-chloroaniline + Ethanoic acid
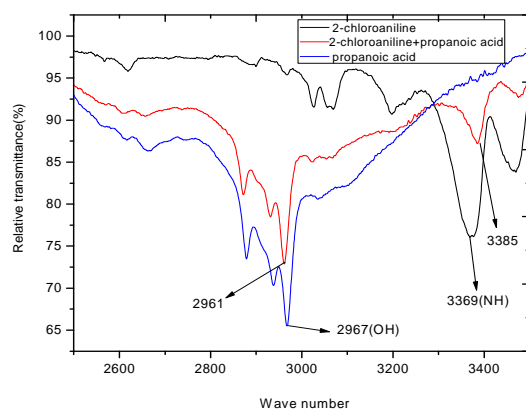
Fig. 4: Infrared spectra of pure 2-chloroaniline, pure propanoic acid and equimolar binary mixture of 2-chloroaniline + Propanoic acid
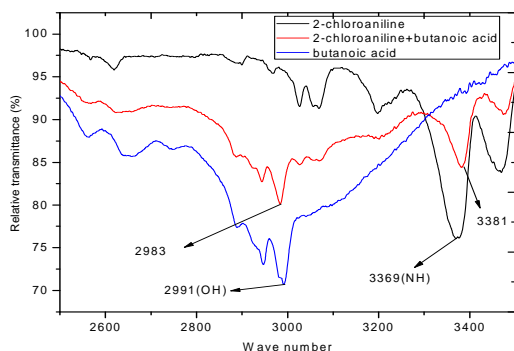
Fig. 5: Infrared spectra of pure 2-chloroaniline, pure butanoic acid and equimolar binary mixture of 2-chloroaniline + Butanoic acid

$$E(2) = q_i \, \frac{F^2(i,j)}{\varepsilon_i - \varepsilon_j} \qquad \text{...(3)}$$

Where q_i is the ith donor orbital frequency, ε_i, ε_j are diagonal elements associated with NBO Fock matrix. The stabilization energy between lone pair electrons (n) of the proton acceptor and antibonding orbitals (σ^*) of the proton donor have been examined for various intermolecular hydrogen bonded complexes [29].

The NBO analysis has been performed here using DFT method to further probe to investigate the relative strength of all hydrogen bonded dimers. The oxygen/nitrogen atom with lone pair acts as donor and X-H(X=N, O) as acceptor in the strong intermolecular charge transfer interaction. The stabilization energies (E (2)) of intermolecular interactions of all dimers were performed by using second order perturbation theory. The stabilization energies between lone pair electrons of proton acceptor and antibonding orbitals of the proton donor have been examined for various intermolecular hydrogen bonds of self-association and cross association at B3LYP/6-311++G(d,p) level theory and tabulated in Table 4.

It is keen to note the point that there is a correlation between hydrogen bond length and stabilization energy E (2), i.e. shorter the bond length (strong hydrogen bond) larger the stabilization energy [30]. In the case of self- association stabilization energy is more in **3** (20.63 KJ.mol^{-1}) and in the case of cross-association the stabilization energy is more in **5** (15.64KJ.mol^{-1}) which concides with the compared results of the interaction energies.

FT-IR analysis

In order to examine the presence of hydrogen bond interaction between N-H and O-H groups of the both the systems, the infrared spectra are recorded at room temperature (298.15 K). Observing the experimental FT-IR spectra for the equimolar binary mixture of (2-chloroaniline +Ethanoic acid), there is a shift of 20 cm^{-1} wave number in the position of –NH and 16 cm^{-1} wave number in the position of –OH for the mixture compared with their respective pure spectrums (Fig.

3).The FT-IR spectra for the equimolar binary mixture (2-chloroaniline+Propanoic acid) there is a shift of 16 cm^{-1} wave number in the position of –NH and 6 cm^{-1} wave number in the position of –OH for the mixture compared with their respective pure spectrums (Fig. 4). Similarly, the FT-IR spectra for the equimolar binary mixture (2-chloroaniline +butanoic acid) there is a shift of 12 cm^{-1} wave number in the position of –NH and 8 cm^{-1} wave number in the position of –OH for the mixture compared with their respective pure spectrums (Fig. 5) .These shifts are caused by the strong intermolecular interactions like hydrogen bonding between the O-H group of carboxylic acids (ethanoic acid, propanoic acid and butanoic acid) and N-H group of 2-chloroaniline. Thus, the FT-IR analysis convinces intermolecular hydrogen bonding of the equimolar binary mixture in both the systems effectively with proportionate variations in stretching wave numbers of –NH and –OH compared to their respective pure components [31].

CONCLUSIONS

In this study we have investigated the hydrogen bond interaction between 2-chloroaniline and carboxylic acid complexes using density functional theory at basis set of 6-311++G (d, p).

From the study of optimized geometries and interaction energies reveals that, among all the dimers considered, **3** (O2-H11…O1) is found to be the most stable one in self-association and **5** (O2-H10….N1) is most stable in cross-association. The AIM analysis of the topological parameters viz., electron density and Laplacian electron density between 2-chloroaniline- carboxylic acid complexes are Hydrogen bonds .The stabilization energy E (2) calculated in NBO method indicates O-H…N hydrogen bonds are stronger among all the dimers.

REFERENCES

1. Scheiner S; Hydrogen Bonding: A Theoretical Perspective, Oxford University Press, New York, (1997).
2. Jeffrey G.A and Saenger W, Hydrogen Bonding in Biological structures, Springer-Verlag, New York, (1994).
3. Desiraju G.R, Steiner T, The weak hydrogen bond: in structural chemistry and biology. Oxford University Press, New York, (1999).
4. Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253–4264.
5. Melandri, S.; Sanz, M.E.; Caminati, W.; Favero, P.G; Kisiel, Z. *J. Am. Chem. Soc.* **1998,** *120,*11504–11509.
6. Scheiner S. Molecular Interactions: From Vander Waals to Strongly Bound Complexes, John Wiley & Sons, England, (1997).
7. Roohi, H.; Nowroozi, A.R.; Anjomshoa, E. *Comput. Theor. Chem.* **2011,** 965, 211-220.
8. Bandyopadhyay, I.; Lee, H.M.; Kim, K.S. *J. Phys. Chem. A.* **2005,***109*, 1720–1728.
9. Parthasarathi, R.; Subramanian, V.; Sathyamurthy, N. *J. Phys. Chem. A.***2006**, *110*, 3349-3351.
10. Hadzi D. Theoretical Treatment of Hydrogen Bonding, John Wiley and Sons, England, (1997)
11. Shishkin, O.V.; Konovalova, I.S.; Gorb, L. *J. Leszczynski, Struct. Chem.***2009**, *20, 37*-41.
12. Karthika, M.; Senthilkumar, L.; Kanakaraju, R. *Comput. Theor. Chem.***2012,** *979*, 54-63.
13. Sewnarain, R.; Raal, J.D.; Ramjugernath, D. *J. Chem. Eng. Data.* **2002**, *47*,603-607.
14. Bruice P.Y. Organic Chemistry. Prentice Hall, New Jersey, (1998).
15. Pereiro, A.B.; Rodriguez, A. *J. Chem. Thermodyn.* **2008,** *40*, 1282-1289.
16. Toumi, A.; Bouanz, M. *J. Mol. Liq.* **2008**, *139*,

55-60.

17. Abdulagatov, I.M.; Tekin, A.; Safarov, J.; Shahverdiyev, A; Hassel, E. *Int. J Thermophys.* **2008**, *29*, 505-533.

18. Zhengyu, Z.; Dongmei, D. *J. Mol. Struct. (Theochem).* **2000,** *505*, 247-255.

19. Zhengyu, Z.; Aiping, F.; Dongmei, D. *J. Quant. Chem.* **2000**, *78*, 186-189.

20. Becke, A.D. *Phys. Rev. A* **1988**, *38*, 3098-3100.

21. Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785-789.

22. Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

23. Frisch, M.; Gaussian 09 (Revisions A. 02). **2009**, Gaussian, Inc., Walling ford CT, USA.

24. Boys, S.F.; Bernardi, F.; *Mol. Phys.* **1970**, *19*, 553–566..

25. Chang, Guo.; Hui, Fang.; Rong-Yi, Huang.; Heng, Xu.; Gen-Hua, Wu.; Shi-Yong, Ye.; *Chem.Phys. Letters* **2013**, *588*, 97-101.

26. Bondi, A.; *J. Phys. Chem.* **1964**, *68*, 441-451.

27. Huang, R. Y.; Du, R.B.; Liu, G. X.; Zhao, X. Q.; Ye, S.Y.; Wu, G. H. *J. Chem. Thermodyn.* **2012**, *55*, 60-66.

28. Zhao, Jun.; Khalizov, Alexei.; Zhang, Renyi. *J. Phys. Chem. A*, **2009**, *113*, 680-689.

29. Weinhold, F.; Landis, C. R. *Chemistry Education Research and Practice*, **2001,** *2*, 91–104.

30. Pal. S.; Kundu, T. K. *ISRN Physical Chemistry* . **2012**, *2012*, 1-12.

31. Trenjado, J.L.; Matos, .J.S.; Alcalde, R. *Fluid phase Equilib.* **2002**, *200*, 295-315.