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Study of Intermolecular Interactions between 2-Chloroaniline Isomeric Butanol Complexes in Gas Phase by Using DFT, NBO, QTAIM and RDG Analysis

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Density functional theoretical (DFT) studies on intermolecular hydrogen bond interactions between self and cross-associated molecular complexes of 2-chloroaniline and isomeric butanols (*e.g.*, 2-methyl-2-propanol, 2-methyl-1-propanol, 2-butanol and1-butanol) have been analyzed in gas phase. Thirteen 2-chloroaniline isomeric butanol complexes are analyzed at B3LYP/6-311++G(d,p) level regarding their geometries, bond characteristics and interaction energies. The second-order perturbation stabilization energy has been calculated by natural bond orbitals analysis. Barder's quantum theory of atoms in molecules are employed to elucidate electron density (ρ) as well as its Laplacian ($\nabla^2\rho$) of the complexes. Further to evaluate the strong and weak interactions between the selected molecular complexes non-covalent interactions plots we used the reduced gradient method.

Keywords: 2-Chloroaniline, Isomeric butanols, Hydrogen bonding, Natural bond orbital, Non-covalent interactions, DFT.

INTRODUCTION

In recent years, large number of theoretical studies has been devoted to explanation of intermolecular hydrogen bonding interactions between the molecular systems [1-6]. Hydrogen bond due to its stability, directionality and dynamics plays a prominent role salvation process [7,8], chemical and biological process, supramolecular chemistry [9,10]. The understanding of hydrogen bonding interactions in the molecular systems is useful to analyze the structure of various biomolecules, biochemical process and molecular recognition.

Intermolecular interactions play an imperative role in studying the structures and physico-chemical properties of the organic molecular systems. So various quantum mechanical methods are essential to calculate structural features, energies and electronic properties of hydrogen bonded systems. Based on the quantum mechanical study of interaction various molecular devices, nanomterials and novel functional molecules can be developed. Generally, present selected molecular systems for investigation having a variety of commercial applications. 2-Chloroaniline has vast industrial importance, which include in oil solvents, fungicides and an intervening agent in the synthesis of azo dyes, agricultural chemicals and prescription drugs and also used in petroleum solvents. Isomeric butanols are widely used in aviation, textile, food, medicine, automotive surface coatings and petroleum industries.

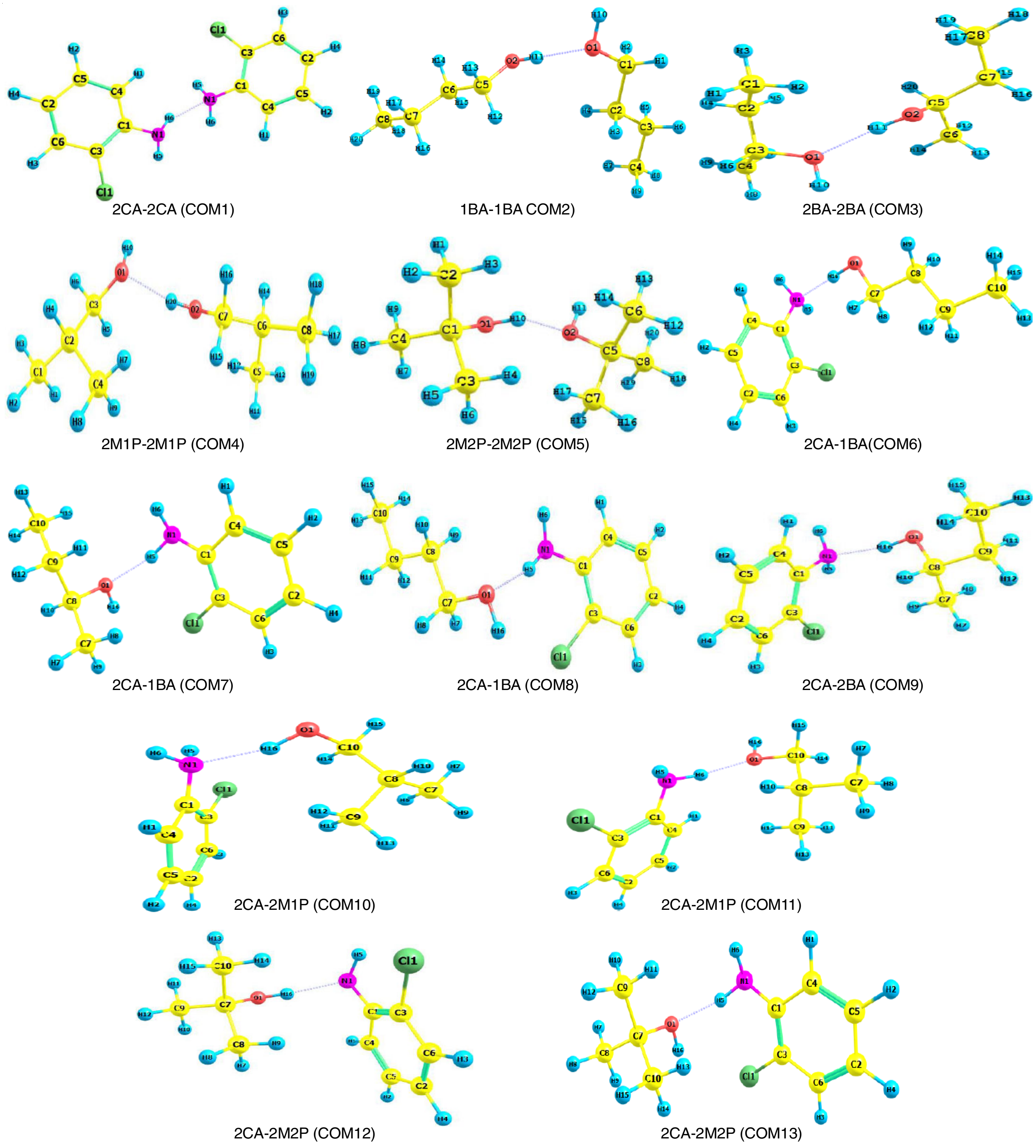
In continuation of our previous report [11] we investigated the influence of position of -CH_3 groups in butanols which forms hydrogen bonding interactions with 2-chloroaniline. To analyze H-bonding microscopically the geometrical parameters ($\Delta R_{X...H}$, $R_{H...Y}$, $\Delta R_{H...Y}$) interaction energies (ΔE_{cp}), second-order perturbation stabilization energies [E(2)] and charge densities ($\rho, \nabla^2\rho$) are studied by using DFT in gas phase.

COMPUTATIONAL METHODS

The main objective of DFT simulations is to analyze the intermolecular interaction between 2-chloroaniline and isomeric butanol complexes in gas phase. The geometrical parameters, interactions energies and second-order perturbation stabilization energies were carried by using method and with basis set B3LYP/6-311++G(d,p). All these simulations in gas phase were carried out using Gaussian 03. The Barder's Quantum theory of atoms in molecules (QTAIM) analysis were carried out by using Multiwfn program [12] in order to calculate the charge density, Laplacian charge density, total electron energy density at bonding critical point (BCP) to analyze the nature of H-bonding. Furthermore, reduced density gradient (RDG) method was used to analyze the H-bonding between 2-chloroaniline and isomeric butanols.

RESULTS AND DISCUSSION

Geometrical optimization: Thirteen possible self- and cross-associated H-bonded complexes between 2-chloroaniline and isomeric butanols systems are shown in Fig. 1. The optimized structural parameters of self- and cross-associated complexes of 2-chloroaniline and butanols have been calculated at B3LYP/6-311++G(d,p) level of theory and are shown in Table-1.



2CA-2CA (COM1)
1BA-1BA COM2)
2BA-2BA (COM3)
2M1P-2M1P (COM4)
2M2P-2M2P (COM5)
2CA-1BA(COM6)
2CA-1BA (COM7)
2CA-1BA (COM8)
2CA-2BA (COM9)
2CA-2M1P (COM10)
2CA-2M1P (COM11)
2CA-2M2P (COM12)
2CA-2M2P (COM13)

Fig. 1. Optimized structural parameters of self- and cross-associated complexes of 2-chloroaniline and butanols

TABLE-1
DISTANCES (Å) AND ANGLES (°) OF THE HYDROGEN BONDS FOR ALL HYDROGEN BOND ASSOCIATIONS AT B3LYP/6-311++G(d, p)

Complexes	X–H···Y	R(X–H)	ΔR (X-H)	R(H···Y)	ΔR(H···Y)	R(X···Y)	∠XHY
COM1	N2–H11···N1	1.01416	0.00611	2.26065	0.48935	3.24571	168.45
COM2	O2–H20···O1	0.97236	0.0107	2.02296	0.69704	2.98531	175.69
COM3	O2–H20···O1	0.97243	0.01021	2.04414	0.67586	2.99629	174.56
COM4	O2–H20···O1	0.97065	0.00729	2.11378	0.63622	3.03285	167.38
COM5	O1–H1···O2	0.97268	0.00932	2.06960	0.65040	3.01333	168.23
COM6	O1–H16···N1	0.97033	0.00867	1.98212	0.76788	3.01540	166.94
COM7	N1–H5···O1	1.01512	0.00708	2.06799	0.65201	3.05156	162.53
COM8	O1–H16···N1	0.97031	0.00809	1.96177	0.78823	3.02311	163.02
COM9	N1–H5···O1	1.01457	0.00653	2.09109	0.62891	3.09317	169.03
COM10	O1–H16···N1	0.96812	0.00677	1.94912	0.80088	3.02119	161.97
COM11	N1–H6···O1	1.01384	0.00580	2.04350	0.67650	3.05062	171.87
COM12	O1–H16···N1	0.97010	0.00875	1.93304	0.81696	2.87776	163.92
COM13	N1–H5···O1	1.01487	0.00683	2.09245	0.62755	3.09245	168.23

As shown in the Fig. 1 the complexes have intermolecular hydrogen bonds. The H-bonds are formed between hydroxyl group (–OH) of isomeric butanols and $-NH_2$ group of 2-chloroaniline. This study reveals that O–H···N and N–H···O hydrogen bonds are formed between amine group of 2-chloroaniline and hydroxy group of isomeric butanols.

During the hydrogen bond formation the stretching of bond length of the proton donor $\Delta R_{X\text{–}H}$ from its corresponding monomer indicates the strength of the hydrogen bond [13]. Table-1 shows the complex **COM12** have shortest H-bond length 1.93304 Å (O1–H16···N1) between the O-H proton donor of 2-methyl-2-propanol (2M2P) and nitrogen atom of 2-chloroaniline (2CA). The largest change in bond length $\Delta R_{O1\text{–}H16}$ is 0.00932 Å. This shows that **COM12** (2CA + 2M2P) is the strongest and stable H-bond among thirteen complexes. The second shortest and strong H-bond is observed in **COM10** with a bond length of 1.94912 Å and the second largest change in the bond length of proton donor $\Delta R_{O1\text{–}H16}$ is 0.00875 Å in 2-chloroaniline and 2-methyl-1-propanol complex. The largest $\Delta R_{O1\text{–}H16}$ in **COM10** shows the second strongest hydrogen bonding in 2-chloroaniline and 2-methyl-1-propanol complex. Similarly the H-bond present in 2-chloroaniline-2-butanol association of **COM8** is third strong hydrogen bond with a bond length of 1.96177 Å and $\Delta R_{X\text{–}H}$ value is 0.00867 Å. In addition, other H-bond involving between 2-chloroaniline-isomeric butanol complexes should be weaker than above three H- bonds [14].

Further a parameter $\Delta R_{H\cdots Y}$ [15], is defined as $\Delta R_{H\cdots Y} = R_{H_{vwr}} + R_{Y_{vwr}} - R_{H\cdots Y}$, where $R_{H_{vwr}}$ and $R_{Y_{vwr}}$ are the vander Waals radii of hydrogen and electronegative atoms [16]. $\Delta R_{H\cdots Y}$ is the hydrogen bond distance. The value of $\Delta R_{H\cdots Y}$ is used to scrutinize the hydrogen bond strength of the complexes. The largest value of $\Delta R_{H\cdots Y}$ is 0.81696 for **COM12** with OH···N interaction is the strongest hydrogen bond. Based on the resulted values of $\Delta R_{X\text{–}H}$ and $\Delta R_{H\cdots Y}$ the strength of the hydrogen bond are in the order is

COM12 > COM10 > COM8 > COM6 > COM2 >
COM11 > COM3 > COM7 > COM5 > COM9 >
COM13 > COM4 > COM1 >

which shows the 2-chloroaniline + 2-methyl-2-propanol dimer (**COM12**) shows strong interaction by hydrogen bonding between nitrogen atom of 2-chloroaniline and hydrogen atom of 2-methyl-2-propanol. This show the geometrical results are good in agreement with the experimental results [11].

Interaction energy analysis: In order to calculate the interaction energy of the H-bond, the sum of the energies of the two monomers was subtracted from the energy of the molecular complex. The energy difference gives the energy contribution due to the specific hydrogen bond. However, in the energy determination of the X···Y heterodimer, all the orbitals of both X and Y are available to the dimer. As a consequence the basis set of each monomer is extended by the presence of the other, which results in a mathematical lowering of the monomer energies. This is referred to as the basis set superposition error (BSSE) [17]. The counterpoise-corrected interaction energies, ΔE^{cp} for thirteen complexes were computed at B3LYP/6-311++G(d,p) are presented in Table-2.

TABLE-2
INTERACTION ENERGY CORRECTED WITH BSSE (ΔE_{cp}, kJ mol^{-1}) FOR ALL DIMERS AT B3LYP/6-311++G (d,p) LEVEL

Complexes	X–H···Y	ΔE	BSSE	ΔE_{CP}
COM1	N2–H11···N1	-13.59473	1.10	-12.4947
COM2	O2–H20···O1	-21.8671	1.94	-19.9271
COM3	O2–H20···O1	-20.4807	0.78	-19.7004
COM4	O2–H20···O1	-20.4591	0.75	-18.3959
COM5	O1–H1···O2	-19.1459	0.75	-18.3959
COM6	O1–H16···N1	-21.8849	0.91	-22.2703
COM7	N1–H5···O1	-16.7528	1.06	-15.7102
COM8	O1–H16···N1	-24.4359	1.01	-20.5939
COM9	N1–H5···O1	-14.7713	0.96	-15.2457
COM10	O1–H16···N1	-26.8241	2.41	-18.2132
COM11	N1–H6···O1	-18.7668	0.93	-17.8368
COM12	O1–H16···N1	-27.3737	2.39	-24.9837
COM13	N1–H5···O1	-15.0888	1.05	-14.0388

Table-2 shows that for 2-chloroaniline and 2-methyl-2-propanol 1:1 complex (**COM12 – COM13**) the interaction energies are -24.9837 and -10.146 KJ mol^{-1}, respectively. In the case of 2-chloroaniline and 2-methyl-1-propanol 1:1 complex (**COM10 – COM11**) the interaction energies are in the range of -18.2132 to -17.8368 KJ mol^{-1}. The **COM12** of 2-chloroaniline and 2-methyl-2-propanol 1:1 association has larger interaction energy (-24.9837 KJ mol^{-1}) compared to 2-chloroaniline and 2-methyl-1-propanol (**COM10**) due to presence of the shorter O–H···N hydrogen bond (1.98905 Å). This is due to hydrogen atom of hydroxy group in 2-methyl-2-propanol is a little more acidic due to the +E effect of three $-CH_3$ group on the α-carbon atom to a greater hydrogen bond than that of 2-methyl-1-propanol.

The calculated interaction energies for the complexes **COM8 – COM9** of 2-chloroaniline and 2-butanol that involved N–H···O and O–H···N interactions are -20.5939 and -15.2457 KJ mol^{-1}. Finally, in the case of 2-chloroaniline and 1-butanol 1:1 complex (**COM6 – COM7**) the interaction energies are in the range of -22.2703 to -15.7102 KJ mol^{-1}. These results shows the strong H-bond is observed in 2-chloroaniline + 2-butanol mixture compared to 2-chloroaniline + 1-butanol mixture. This is because of presence of two methyl groups ($-CH_3$) increases electron density at oxygen atom of hydroxy group to a greater extent compared to that of 1-butanol. This is in good agreement with the results of geometrical optimization.

Quantum theory of atom in molecular (QTAIM) analysis: QTAIM analysis on 2-chloroaniline and isomeric butanol 1:1 complexes for investigations of intermolecular hydrogen bond interactions was studied at B3LYP/6-311++G(d,p) level of theory. In this QTAIM analysis a chemical bond is characterized by a point called bonding critical point (BCP) with a (3,-1) topology between the atoms connected by a hydrogen bond. The values of electron density [ρ(r)] and Laplacian of the electron density ($\nabla^2\rho(r)$) at BCP of all dimers are summarized in Table-3.

Koch and Popelier [18] proposed three local topological properties to detect and characterize the hydrogen bond.

- Existence of BCP between proton (H) and acceptor (Y) contact is the conformation of formation of H-bond.
- At BCP of the H···Y the electron density (ρ(r)) lies in the range of 0.002-0.040 a.u.
- Laplacian electronic density [$\nabla^2\rho(r)$] is positive and lies in the range 0.015-0.15 a.u.

In the present study the values of ρ(r) and $\nabla^2\rho(r)$ varies from 0.01778 to 0.02632 a.u and 0.06355 to 0.09560 a.u. This shows that the interacting complexes have strong hydrogen bonds. From Table-3, it is observed that the large electron densities are 0.02322 a.u for **COM12** and 0.02228 a.u for **COM10** and 0.02215 a.u for **COM8** and all Laplacian electron density values are positive indicating closed shell interactions [19]. The electron density and H-bond lengths are inversely proportional to each other so, complex **COM12** posses a large electron density 0.02322 a.u with a shortest hydrogen bond length of 1.93304 Å. So the observed values of and for the complexes shows that O–H···N interaction representing the most strong and stable hydrogen bonded complexes.

According to virial theorem the relation between local kinetic energy (K_{BCP}), potential energy density (V_{BCP}) and total electronic energy density (H_{BCP}) is

$$\frac{1}{2}\nabla^2\rho(r)_{BCP} = 2K_{BCP} + V_{BCP}$$

$$H_{BCP} = K_{BCP} + V_{BCP}$$

The sign of H_{BCP} at BCP is an index to determine whether the molecular interactions are electrostatic (H > 0) or covalent (H < 0) in nature. According to Grabowski *et al.* [20] Laplacian of the electron density $\nabla^2\rho(r)$ and total electronic energy density H_{BCP} are used as criteria at BCP of hydrogen bond:

- For weak and medium hydrogen bonds both $\nabla^2\rho(r)$ and $H_{BCP} > 0$.
- For strong hydrogen bonds $\nabla^2\rho(r) > 0$ and $H_{BCP} < 0$.
- For very strong hydrogen bonds both $\nabla^2\rho(r)$ and $H_{BCP} < 0$.

From Table-3 both the vales of $\nabla^2\rho(r)$ and H_{BCP} at BCP indicating the interactions are weak hydrogen bonds and electrostatic nature is present in all the complexes [21].

NBO analysis: The interaction between occupied Lewis type (donor) NBO's to unoccupied non-Lewis type (acceptor) NBO's can be described as a hyper conjugative electron transfer process from the donor to acceptor orbital. The second-order perturbation stabilization energy for proton donor- acceptor interaction relevant to hydrogen bond formation in 2-chloroaniline and isomeric butanols complex from NBO analysis at B3LYP/6-311++G(d,p) level of theory and are summarized in Table-4. From Table-4 in the self-associated 2-chloroaniline complex (**COM1**) the major interaction is that N (amino group) offers its lone pair to the $\sigma(N-H)^*$ antibond; this interaction stabilizes the system with energy 19.83 kcal mol^{-1}.

TABLE-3
TOPOLOGICAL PARAMETERS FOR BONDS OF INTERACTING ATOMS OF DIMERS: ELECTRON DENSITY (ρ_{BCP} (a.u.)), LAPLACIAN OF ELECTRON DENSITY ($\nabla^2\rho_{BCP}$ (a.u.)), ELECTRON KINETIC ENERGY DENSITY (G_{BCP} (a.u.)), ELECTRON POTENTIAL ENERGY DENSITY (V_{BCP} (a.u.)), TOTAL ELECTRON ENERGY DENSITY (H_{BCP} (a.u.)) AT BOND CRITICAL POINT (BCP)

Complex	Interactions	(ρ_{BCP} (a.u.)	$\nabla^2\rho_{BCP}$ (a.u.)	V_{BCP} (a.u.)	K_{BCP} (a.u.)	H_{BCP} (a.u.)
COM1	N2–H11···N1	0.01901	0.06912	-0.013281	0.015301	0.00202
COM2	O2–H20···O1	0.02632	0.09560	-0.020134	0.022018	0.00188
COM3	O2–H20···O1	0.02469	0.09492	-0.018958	0.021345	0.00238
COM4	O2–H20···O1	0.02587	0.09236	-0.019543	0.021318	0.00177
COM5	O1–H1···O2	0.02520	0.09000	-0.018783	0.020642	0.00185
COM6	O1–H16···N1	0.01978	0.06925	-0.013277	0.015295	0.00201
COM7	N1–H5···O1	0.01422	0.06355	-0.012567	0.014228	0.00166
COM8	O1–H16···N1	0.02215	0.66648	-0.013662	0.015162	0.00150
COM9	N1–H5···O1	0.01782	0.06442	-0.011768	0.013937	0.00216
COM10	O1–H16···N1	0.02228	0.06739	-0.013792	0.015320	0.00152
COM11	N1–H6···O1	0.01997	0.07367	-0.013739	0.016080	0.00234
COM12	O1–H16···N1	0.02322	0.06969	-0.014594	0.016009	0.00141
COM13	N1–H5···O1	0.01778	0.06435	-0.011790	0.013939	0.00214

TABLE-4
SECOND ORDER PERTURBATION THEORY ANALYSIS OF THE FOCK MATRIX IN THE NBO BASIS FOR THE INTERMOLECULAR INTERACTIONS FOR DIMERS

Complex	Donor NBO(i)	Acceptor NBO(j)	E(2) (kJ/mol)
COM1	LP(1) N1	BD*(1)N2-H10	19.83
COM2	LP (1) O1	BD*(1)O2-H11	8.49
	LP (2) O1	BD*(1)O2-H11	30.75
COM3	LP (1) O1	BD*(1)O2-H11	20.45
	LP (2) O1	BD*(1)O2-H11	12.46
COM4	LP (1) O1	BD*(1)O2-H11	6.06
	LP (2) O1	BD*(1)O2-H11	29.87
COM5	LP(1) O1	BD*(1) N -H1	8.07
	LP(2) O1	BD*(1) N1-H1	26.17
COM6	LP (1) N1	BD*(1) H16-O1	28.07
COM7	LP(1) O1	BD*(1) N1-H5	13.46
	LP(2) O1	BD*(1) N1-H5	3.52
COM8	LP (1) N1	BD*(1) H10-O1	32.45
COM9	LP(1) O1	BD*(1) N1-H6	12.53
	LP(2) O1	BD*(1) N1-H6	2.81
COM10	LP (1) N1	BD*(1) H10-O1	33.33
COM11	LP(1) O1	BD*(1) N1-H6	13.97
	LP(2) O1	BD*(1) N1-H6	3.59
COM12	LP (1) N1	BD*(1) H16-O1	38.52
COM13	LP(1) O1	BD*(1) N1-H5	14.82
	LP(2) O1	BD*(1) N1-H5	2.82

Whereas in isomeric butanols complexes (**COM2–COM5**) the major interaction are the oxygen atom offers their p electrons to the $\sigma(O–H)^*$ and these interaction stabilizes the systems with energies lies between 6.06-30.75 kcal mol^{-1}. The orbital interactions $LP(O) \rightarrow \sigma(N–H)^*$, $LP(N) \rightarrow \sigma(O–H)^*$ in 2-chloroaniline and 1-butanol complexes (**COM6–COM7**) have second-order perturbation stabilization energy E (2) range of 13.46-28.07 kcal mol^{-1}. Whereas the orbital interactions $LP(O) \rightarrow \sigma(N–H)^*$, $LP(N) \rightarrow \sigma(O–H)^*$ in 2-chloroaniline and 2-butanol complexes (**COM8–COM9**) having stabilization energy E (2) in range of 12.53-32.45 kcal mol^{-1}. The orbital interactions $LP(O1) \rightarrow \sigma(N1\text{-}H5)^*$, $LP(N1) \rightarrow \sigma(O1\text{-}H15)^*$ in 2-chloroaniline and 2-methyl-1-propanol complexes (**COM10 – COM11**) have second-order perturbation stabilization energies E(2) are 13.97-33.33 kcal mol^{-1}. Finally in 2-chloroaniline and 2-methyl-1-propanol complexes (**COM12 – COM13**) the perturbation stabilization energies E (2) are 14.82-38.52 kcal mol^{-1}.

Among the thirteen hydrogen bonded dimers 2-chloroaniline and 2-methyl-2-propanol dimers exhibit strongest interaction between lone pair electrons of the proton acceptor n (O1) and anti-bonding orbital's of the proton donor $\sigma^*(N1\text{-}H5)$ of correspond to stabilization energy 38.52 kcal mol^{-1}.

Non-covalent index (NCI) index: Further, to analyze the strength of hydrogen bond interaction between selected dimers (**COM12, COM10** and **COM8**) it is useful to introduce non-covalent index (NCI index).

The NCI index method uses the reduced density gradient (RDG) [22], S(r) defined as:

$$S(r) = \frac{|\nabla\rho(r)|}{2(3\pi)^{1/3}\rho(r)^{4/3}}$$

If weak intermolecular interaction is present, characteristic spikes are observed on reduced density gradient [S(r)] *versus* sign (λ_2) ρ in the low-density region of component molecules. The RDG curves for three associations (O–H···N) with sharp characteristic spikes are shown in Fig. 2 with isosurfaces s = 0.50. The characteristic spikes at negative indicating the presence of non-covalent interactions, whereas peaks at positive indicating repulsive and the peaks nearer to zero indicating vander Waals interaction.

Form Fig. 2, the heterodimer of 2-chloroaniline (2CA) and 1-butanol (1BA) (**COM6**) is connected *via* O-H···N hydrogen bond with two low-reduced gradient spikes are at low density lies at -0.0302005and -0.0141831 a.u. In **COM6** characteristic spikes very near zero, indicating weak hydrogen bond interaction. Fig. 2 shows the hetrodimer of 2-chloroaniline and 2-butanol (2BA) (**COM8**) low-reduced gradient spike is at low density lies at -0.039063568 a.u. Fig. 2 shows the dimer **COM10** of 2-chloroaniline and 2-methyl-1-propanol (2M1P) is connected *via* O–H···N (blue region) hydrogen bond with two low-reduced gradient spikes are at low density lies at -0.040111 and -0.0150262 a.u. Finally for the complex **COM12** of 2-chloroaniline and 2-methyl-2-propanol (2M2P) low-reduced gradient spike is at low density lies at -0.0409546 a.u are shown in Fig. 2. So the stability of hydrogen bonds in cross-associated complexes follows the order as **COM12 > COM10 > COM8 > COM6**, which in agreement with the QTAIM analysis.

Conclusion

The intermolecular interactions between the self and cross-associated structures of 2-chloroanilie-isomeric butanols complexes have been analyzed by density functional method (DFT) at B3LYP/6-311++G (d, p) level theory. The study of optimized geometries, interaction energies, quantum theory of atom in molecule (QTAIM) and natural bonding (NBO) theory reveals that, among all the thirteen self and cross associated dimers **COM12** (2-chloroaniline-2-methyl-1-propanol) with O–H···N hydrogen is found to be the most stable complex.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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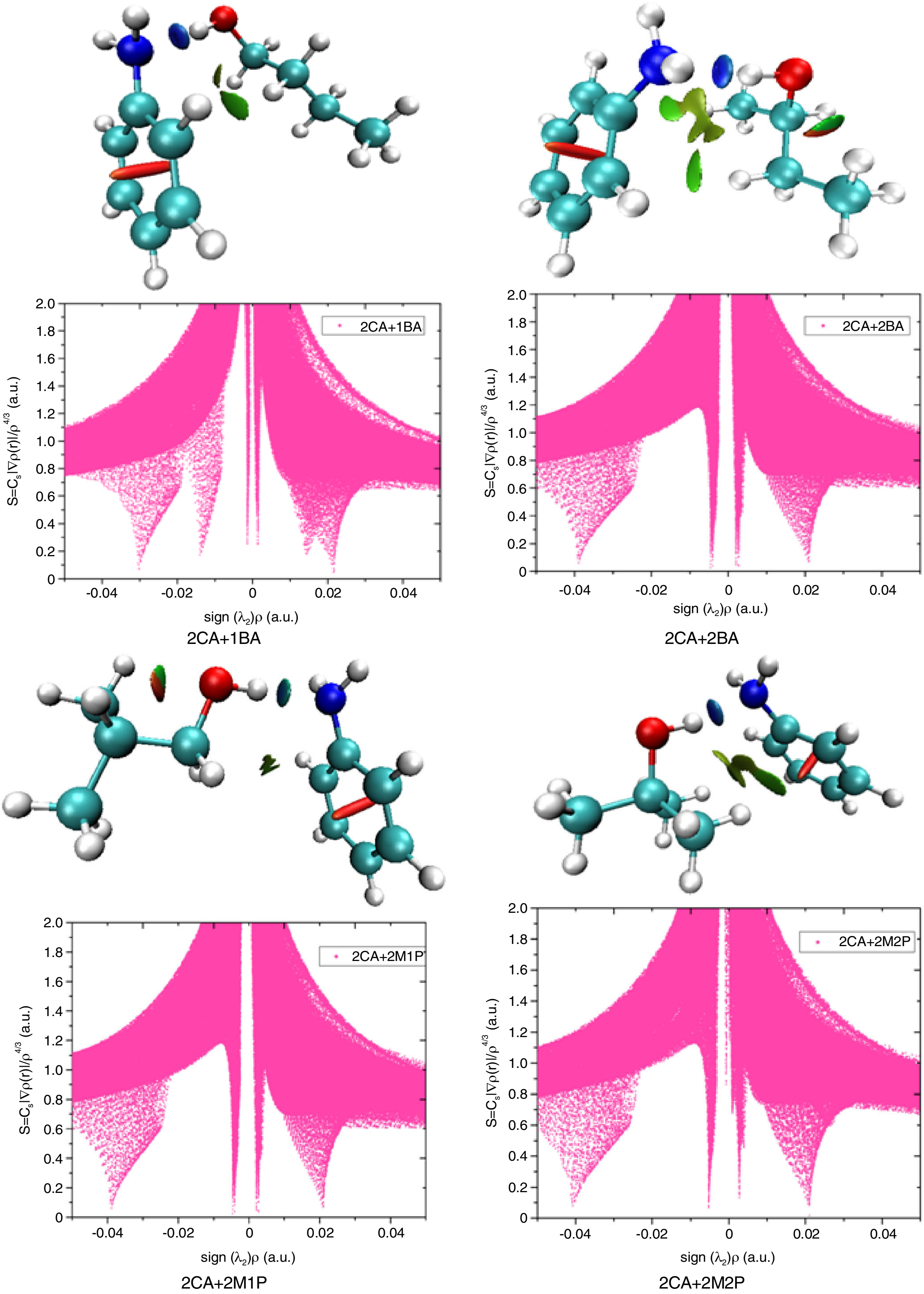

2CA+1BA 2CA+2BA

2CA+2M1P 2CA+2M2P

Fig. 2. Plots of reduced density gradient *versus* electron density multiplied by the sign of second hessian eigen values and gradient isosurfaces with s = 0.5 a.u. for hydrogen bond association of 2-chloroaniline + isomeric butanols. The surfaces are colored on a blue-green-red scale according to values of sign(λ_2)ρ ranging from -0.03 to 0.02 a.u.

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