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Theoretical Characterization of Hydrogen Bonding Interactions between RCHO (R = H, CN, CF_3, OCH_3, NH_2) and HOR′(R′ = H, Cl, CH_3, NH_2, C(O)H, C_6H_5)

DAMANJIT KAUR* and RAJINDER KAUR
Department of Chemistry, Guru Nanak Dev University, Amritsar 1430 05, India
e-mail: damanjit32@yahoo.co.in; rajinderkaurgill22@gmail.com

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Abstract. In this work, density functional theory and *ab initio* molecular orbital calculations were used to investigate the hydrogen bonded complexes of type RCHO···HOR′ (R = H, CN, CF_3, OCH_3, NH_2; R′ = H, Cl, CH_3, NH_2, C(O)H, C_6H_5) employing 6-31++g** and cc-pVTZ basis sets. Thus, the present work considers how the substituents at both the hydrogen bond donor and acceptor affect the hydrogen bond strength. From the analysis, it is reflected that presence of –OCH_3 and –NH_2 substituents at RCHO greatly strengthen the stabilization energies, while –CN and –CF_3 decrease the same with respect to HCHO as hydrogen bond acceptor. The highest stabilization results in case of (H_2N)CHO as hydrogen bond acceptor. The variation of the substituents at –OH functional group also influences the strength of hydrogen bond; nearly all the substituents increase the stabilization energy relative to HOH. The analysis of geometrical parameters; proton affinities, charge transfer, electron delocalization studies have been carried out.

Keywords. Hydrogen bond; carbonyl; substituent effect; SAPT; AIM; NBO; MESP.

1. Introduction

The hydrogen bonding interactions are the most common, yet very important in three dimensional crystal packing, reactivity of molecules and physical properties of molecules.[1–8] Despite extensive research on the topic, it has been a centre of attraction for further studies as the perception changed from purely electrostatic to partially covalent,[9–11] from conventional polar to nonconventional hydrogen bond (HB) donors,[12–17] from electronegative lone pair bearing HB acceptors to pi cloud as HB acceptors.[18–22] They have been very well characterized by various methodologies including AIM[23–25] (atoms in molecules), NBO[26–28] (natural bond orbital), MESP[29–32] (molecular electrostatic potential), vibrational frequency analysis,[33–35] etc.

The carbonyl compounds including aldehydes, ketones, carboxylic acids, their halogenated derivatives, amides, esters etc are very commonly found in proteins, lipid-membranes and other biologically active compounds like drugs, toxins and penicillin.[36] The hydrogen bonding interactions involving carbonyl functionality are important as being part of peptide functionality.[37] These are important to affect the conformational preference of the biological molecules and hence their properties.[38–40] Their further role in protein structure, folding and stability can be well anticipated.[37,41–43]

There are numerous reports on hydrogen bonded carbonyl complexes by theoreticians and experimentalists[44–61] in the past and even today.[62–68] For example, the earlier work by Bobadova-Parvanova and his co-worker investigated the hydrogen bonded complexes between open-chain substituted aliphatic carbonyl compounds and hydrogen fluoride at the HF/6-31G** level.[50] They analyzed vibrational-frequency and infrared intensity for the isolated and hydrogen-bonded complexes and a linear correlation for the variation of HB strength (ΔE) with H-F stretching frequency shift, change in H-F bond length, molecular electrostatic potential was found. The total energy corrected for the complexes studied was found to vary between −1.48 kcal/mol and −7.53 kcal/mol at HF/6-31G** level. Gu *et al.* have applied infrared-ultraviolet double resonance spectroscopy to study the supersonically cooled gaseous complexes of formic acid, acetic acid, propionic acid, formamide and water with 9-hydroxy-9-fluorenecarboxylic (9HFCA).[62] In the complexes under study each binding partner to 9HFCA can act as both proton donor as well as acceptor. They have calculated the stretching frequencies and analyzed that 9-hydroxy stretch is blue shifted in the complexes of formic acid, acetic and propionic acids, while red shifted in the complexes with formamide and

*For correspondence

water. In addition, density functional calculations have also been applied to explain the above quantitative frequency shift behavior of –OH group of 9HFCA. A recent study by Grabowski *et al.* revisited the "resonance assisted hydrogen bonds" (RAHB) in the dimers of carboxylic acids (formic, acetic, trifluoroacetic acid) and amides (formamide, acetamide and triflouroacetamide) employing modern valence-bond theory, the hybrid variational-perturbational interaction energy decomposition scheme and AIM analysis.[63] The carboxylic acids and amides were chosen to study the intermolecular RAHBs while malondialdehyde along with its derivatives were selected to study intramolecular RAHBs. Their studies on estimated resonance stabilization energies and relative magnitudes from energy decomposition components inferred that charge-delocalization is responsible for origin of stabilization in these dimeric structures. The electrostatic energy is completely compensated by exchange repulsion and therefore, the HBs in the studied complexes are in fact, charge-delocalization assisted rather than resonance assisted. Very recently, Kollipost *et al.* have investigated experimentally and computationally the infrared spectra of methanol and acetone clusters as well as their mixed clusters (i.e., methanol-acetone clusters) up to tetrameric form.[68] The quantum chemical calculations were used to predict their binding energies and these were found to vary from −32.6 kJ/mol for methanol-acetone dimer to −131.5 kJ/mol for methanol-acetone tetramer in the 3:1 ratio at the B3LYP-D3/def2-TZVP level. Their studies inferred that the in case of mixed clusters OH···O=C interaction was strongest in comparison to interaction between alcohol oxygen and methyl hydrogen of acetone. Moreover, they predicted that the former hydrogen interactions were preferred over other self-interactions but presence of more than one alcohol or acetone units in the mixed cluster system led to cooperativity due to polarizations of the OH or C=O groups respectively. Concept of Fermi resonance transmitted through OH···O=C intermolecular bond in case of trimeric complex formed between two methanol and one acetone unit has been suggested to explain the results. Carbonyl complexes with O-H···O=C bonds is also important from the crystallographic point of view.[69–71] For instance, Nguyen *et al.* have analyzed the experimental electron density distribution (EDD) in the cocrystals of salicylic acid with 8-hydroxyquinoline using high resolution X-ray diffraction data.[69] They compared experimental EDD with theoretical densities evaluated using Atoms in Molecules theory using high level ab initio and BHandH calculations. They found that salicylic acid crystallizes in the triclinic crystal system and the number of inter- and intramolecular interactions including C···C, O···C and N···C (π-π) type of interactions are present within one asymmetric unit of neutral salicylic acid molecule, a salicylate anion, and an 8-hydroxyquinolinium cation. The intramolecular HBs in each salicyl moieties were observed between phenolic OH and the carboxy group. The topological analysis indicated that all three types of interactions were of 'closed-shell' type and the critical points obtained experimentally were found to be absent in theoretical analysis which indicates some discrepancies associated with multipole model for weak and long-range interactions (π-π). They have also obtained energy of π-π interactions and a good agreement between the relative energy with the strength of π-stacking derived from Espinosa approach was found.

The principal thrust of the present paper is an elucidation of how RCHO···HOR′ interaction is affected by the substituents on the carbonyl functionality, C=O as HB acceptor and on the O-H bond as HB donor. Here, the substituents examined on C=O bond include CN, CF_3, OCH_3 and NH_2 and the features are compared relative to unsubstituted carbonyl HCHO. The various substituents attached to O-H bond acting as HB donor are H, Cl, CH_3, NH_2, HC=O and C_6H_5. The properties discussed in this article are the stabilization energies, geometrical parameters, frequency shifts; AIM (atoms in molecules), NBO (natural bond orbital), SAPT (symmetry adapted perturbation theory) and MESP (molecular electrostatic potential) analyses with aid of ab inito molecular orbital (MO) and density functional theory (DFT) methods.

2. Computational

The geometries of all the monomers and the corresponding hydrogen bonded complexes were fully optimized by means of ab initio molecular orbital and density functional methods. The 6-31++G** and cc-pVTZ basis sets was employed for both the methods. All of the gas-phase structures were characterized as potential energy minima at the same theoretical level verifying that all the vibrational frequencies are real. The stabilization energy (ΔE) was estimated as difference between the total energy of the complex and the sum total of the monomers. The basis set superposition error (BSSE) was eliminated by the counterpoise method proposed by Boys and Bernadi.[72] Atomic charges were computed by using natural population analysis (NPA) at the MP2/cc-pVTZ level. Gaussian 09 suite of program[73] was employed for all of the computations. The second order stabilization energies ($E^{(2)}$) were also analyzed at the MP2/cc-pVTZ level using

the NBO program under Gaussian 09 package.[74] To decompose interaction energy into its components, the SAPT was performed at the MP2/cc-pVTZ level with the use of GAMESS package which was interfaced to the SAPT2008.2 code.[75–77] The topological properties of electron density at the bond critical points (bcps) was studied using AIM methodology[78–80] which employs AIM2000 program.[81] The MESP analysis[82,83] of the monomers was carried out at the MP2/cc-pVTZ level. MESP at each atom of the HB acceptor and donor molecules was obtained from the standard output of the Gaussian 09 program.

3. Results and discussions

3.1 *Stabilization energies*

Figure 1 shows the optimized structures of RCHO···HOR′ complexes at MP2/cc-pVTZ level. Table 1 presents the stabilization energies for the hydrogen bonded complexes of the carbonyl compounds at B3LYP/6-31++G**, MP2/6-31++G** and MP2/cc-pVTZ levels. The stabilization energies with BSSE correction at the latter level will be used in the discussion. It has been observed that the stabilization energies evaluated at MP2/cc-pVTZ are consistently higher than the values obtained at MP2/6-31++G** whereas the values are comparable to B3LYP/6-31++G** theoretical method. From table 1, it is apparent that the BSSE-corrected stabilization energies are computed to be within a range of 4.22–8.91 kcal/mol for the HCHO complexes at MP2/cc-pVTZ theoretical level. The stabilization energy of complex of HCHO with HOC(O)H is highest among all the complexes of formaldehyde. The stabilization energies follows the order HCHO···HOH < HCHO···$HOCH_3$ < HCHO···$HONH_2$ < HCHO···HOC_6H_5 < HCHO···HOCl < HCHO···HOC(O)H. Single hydrogen bond (HB) is located in the complexes HCHO···HOCl, HCHO···$HOCH_3$ and HCHO···HOC_6H_5 while the complexes HCHO···HOH, HCHO···$HONH_2$ and HCHO···HOC(O)H show the presence of two HBs. With carbonyl oxygen as HB acceptor and formyl C-H as HB donor, the difference in the latter set of complexes is the size of cyclic structure and the stabilization energies. Thus, the substituents –Cl, $–CH_3$, $–NH_2$, –HC=O and $–C_6H_5$ at the HB donor group O-H increase the stabilization energy of complex formation relative to HOH as reference. Though the complexes show multiple hydrogen bonding interactions in several cases but such pairing can be expected to be preferred in gas phase. In crystal phase, multiple hydrogen bonding interactions along with other intermolecular interactions exist but not necessarily between two neighbouring units. The multiple interactions between different monomeric units in solid state are important for final crystal structure but there are few reports where dimeric units with two HBs have been observed in crystalline state as well. In a similar report by Desiraju *et al.*, the role of substituent groups on the formation of dimers and catemers in case of phenylpurvic acid have been studied. Steric effect of the substituent in restricting the product to dimeric form have been stressed.[71,84]

The role of substituents at the carbonyl functionality on the stability of complex formation has also analyzed by substituting one of the hydrogen of carbonyl group (H_2C=O) by –CN, $–CF_3$, $–OCH_3$ and $–NH_2$. As can be seen from the table that the presence of substituents $–OCH_3$ and $–NH_2$ at the HB acceptor carbonyl group enhances the stabilization energy while the presence of substituents –CN and $–CF_3$ diminishes the values. Similar inference has also been drawn by Kim *et al.* in their study on substituent effect of N,N-dialkylamides on intermolecular hydrogen bonding with thioacetamide in CCl_4 solvent using theoretical and experimental techniques.[85] Their studies showed that stability of the hydrogen-bonded complex between thioacetamide and amides had increased with increase in electron-donating alkyl group. The HB acceptor ability have often been linked to proton affinity of that site. The proton affinity values of the carbonyl compounds RCHO under study are evaluated and are listed in table 2. The experimental values[86,87] wherever available are also included in the table. The plot of stabilization energies of the complexes RCHO···HOC(O)H versus proton affinity of the HB acceptors RCHO (R = H, CN, CF_3, OCH_3, NH_2) shows a linear correlation with R^2 ranging in 0.943 (figure 2).

3.2 *Geometrical parameters and frequency shifts*

In table 3, we collect the HB distances, HB angles, and the changes in the O-H bond length of HB donor upon complex formations at the MP2/cc-pVTZ level. The complexes HCHO···HOCl, and HCHO···$HOCH_3$ have single HB with distances 1.804 and 1.970 Å respectively. In the most stabilized complex HCHO···HOC(O)H, the two HBs have carbonyl of both the monomeric units as HB acceptor but the geometrical parameters suggest O1···H5-O6 HB to be stronger in comparison to O8···H4-C2 HB. The strongest hydrogen bonding ability of HOC(O)H is also apparent in the complexes involving substituted RCHO molecules and is understandable with both HB acceptor (C=O) and HB donor (O-H) being of classical nature. The comparison of values also reflects that -OH of formic acid serves as better HB donor relative to -OH of alcohols (CH_3OH,

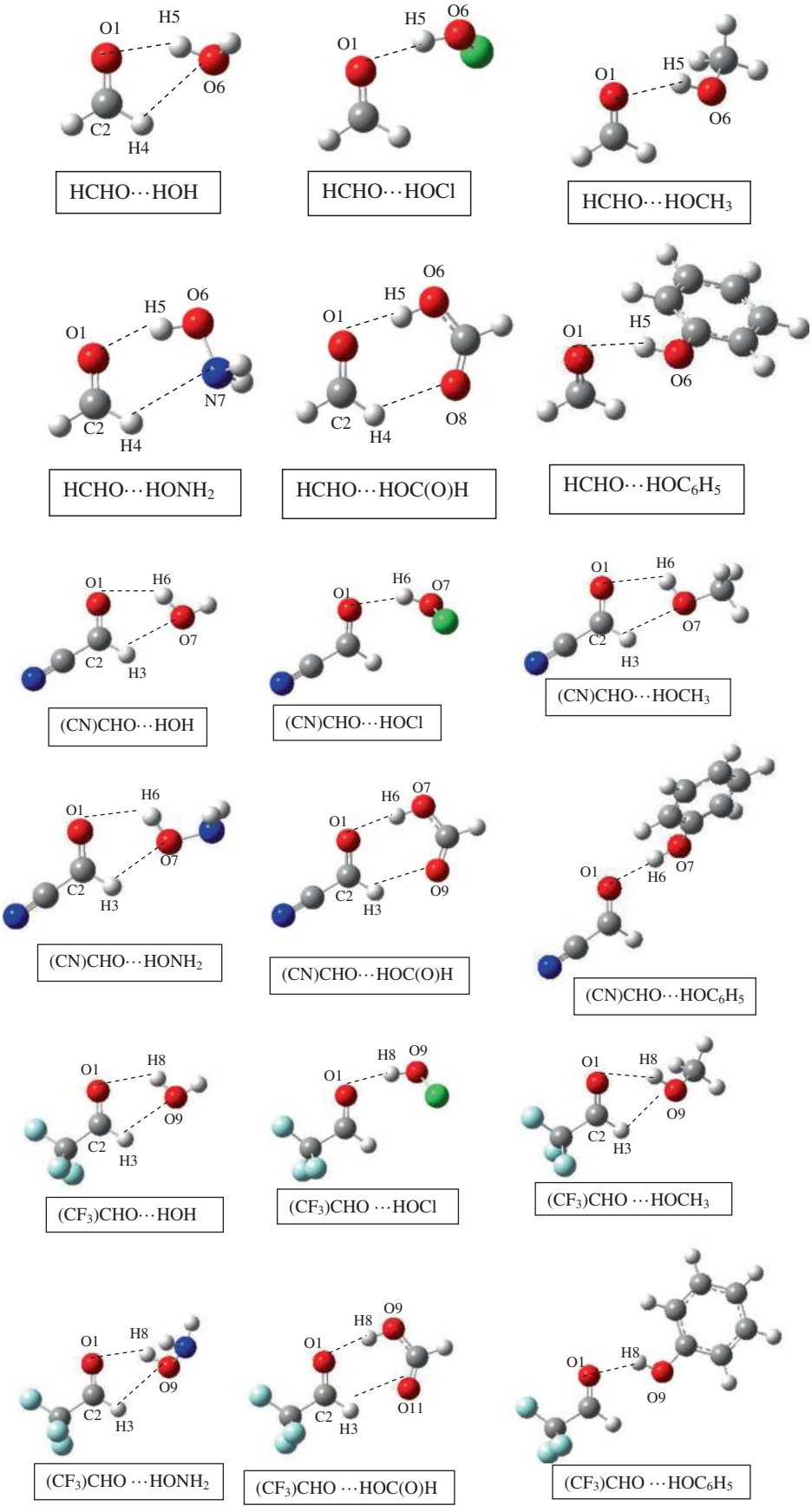

Figure 1. Optimized complexes of carbonyl compounds with HOR′ (R′ = H, Cl, CH_3, NH_2, C(O)H, C_6H_5) donor molecules at MP2/cc-pVTZ level.

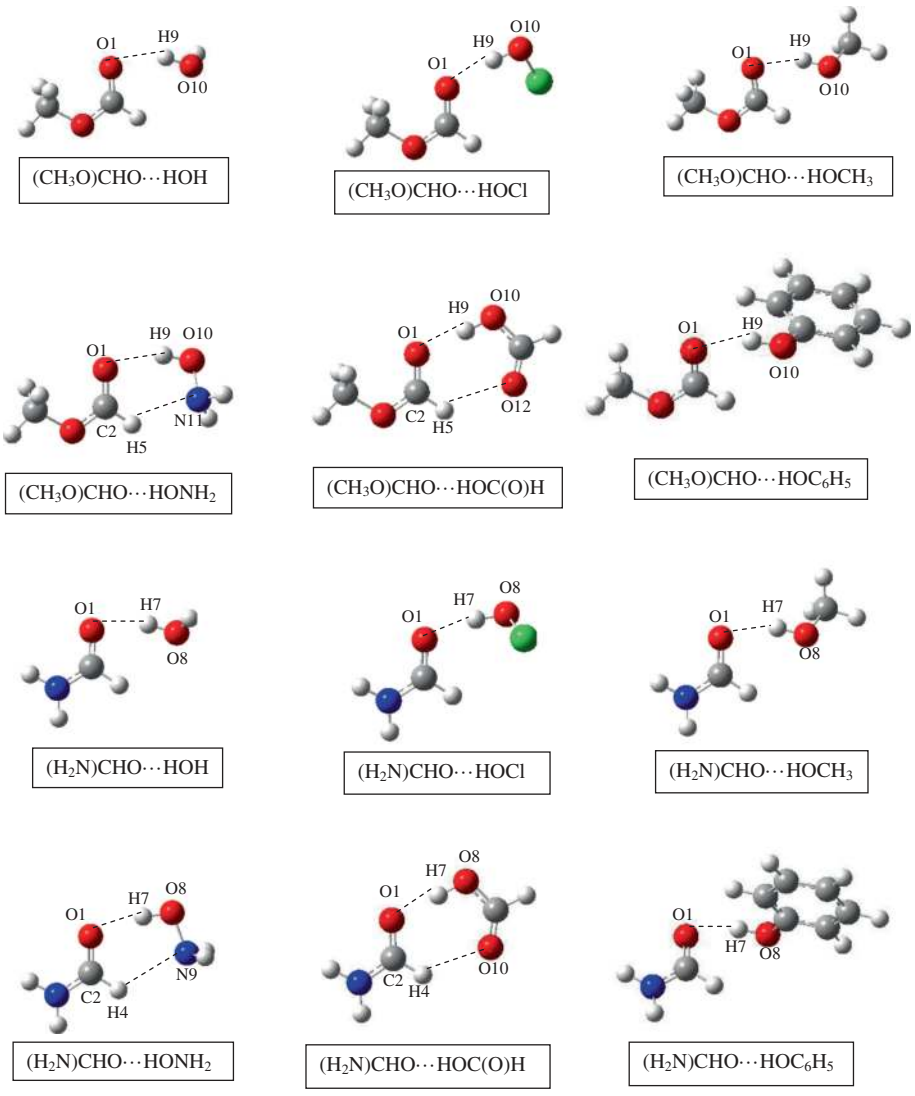

Figure 1. (continued)

NH_2OH, C_6H_5OH). Similar inference from the crystallographic data has also been obtained by Moorthy *et al.* in their recent communication.[88] The complex $HCHO\cdots HOC_6H_5$ is adorned with single HB only with distance 1.903 Å with phenol as the HB donor. The crystal structure of 1,3,5-triaroylbenzene (TAB) having phenol residue at its periphery had also shown similar type of binding highlighting the importance of such HBs in crystal engineering.[89] In the TAB.EtOAc crystal structure, each TAB were attached to six adjacent units via O-H···O=C type of HBs with intermolecular distances ranges between 2.678–2.690 Å and the phenol molecule only serve as HB donor.

With the presence of the substituents –CN and $-CF_3$ at the carbonyl group, the elongation of O···H-O HB distance is indicated in the complexes and relatively larger deviation from linearity of the HB angles is also reflected; as a consequence of which the stabilization energies associated with the complex formation are reduced in these. On the other hand, the complexes involving $-OCH_3$ and $-NH_2$ substituted RCHO as HB acceptor, the O···H intermolecular distances were observed to be shorter in comparison to respective complexes with HCHO, and thus the increase in stabilization energies of the respective complexes is reflected. As can be seen from the figure 1 that three of the complexes with $HONH_2$ have N as HB acceptor towards C2-H of HCHO, $(CH_3O)CHO$ and $(H_2N)CHO$ whereas in two complexes involving (CN)CHO and $(CF_3)CHO$ have O of $HONH_2$ as HB acceptor. The presence of two HBs in any complex leads to cyclic structure that causes the HB angle to deviate from linearity. In most of the cases, the large deviation from linearity is reflected except in the complexes RCHO···HOC(O)H. Deviation from linearity is also reflected in the complexes with single HB, may be arising due to favorable alignments of the dipoles in the monomeric units.

Table 1. Stabilization energies (ΔE, kcal/mol) for the RCHO···HOR′ hydrogen bonded complexes at B3LYP/6-31++G**, MP2/6-31++G**, and MP2/cc-pVTZ levels.

	Stabilization energies (-ve)		
Complexes	ΔE_{B3LYP}	ΔE_{MP2}	$\Delta E_{cc-pVTZ}$
HCHO···HOH	4.55	4.67	4.22
HCHO···HOCl	6.36	5.90	6.48
HCHO···$HOCH_3$	4.83	4.78	4.40
HCHO···$HONH_2$	5.29	5.22	5.38
HCHO···HOC(O)H	8.98	8.31	8.91
HCHO···HOC_6H_5	5.51	5.65	6.13
(CN)CHO···HOH	4.39	4.59	4.18
(CN)CHO···HOCl	4.26	4.11	4.69
(CN)CHO···$HOCH_3$	4.43	4.72	4.22
(CN)CHO···$HONH_2$	4.43	4.80	4.31
(CN)CHO···HOC(O)H	7.84	7.35	7.63
(CN)CHO···HOC_6H_5	4.09	4.58	4.67
(CF_3)CHO···HOH	4.07	4.35	3.81
(CF_3)CHO···HOCl	4.39	4.05	4.66
(CF_3)CHO···$HOCH_3$	4.07	4.46	3.87
(CF_3)CHO···$HONH_2$	4.15	4.51	3.93
(CF_3)CHO···HOC(O)H	7.46	7.03	7.42
(CF_3)CHO···HOC_6H_5	3.94	4.31	4.47
(CH_3O)CHO···HOH	4.89	4.89	4.46
(CH_3O)CHO···HOCl	7.44	6.50	7.57
(CH_3O)CHO···$HOCH_3$	5.15	4.79	4.73
(CH_3O)CHO···$HONH_2$	5.67	5.34	5.63
(CH_3O)CHO···HOC(O)H	9.81	9.00	9.78
(CH_3O)CHO···HOC_6H_5	6.29	6.06	6.37
(H_2N)CHO···HOH	6.51	6.18	5.72
(H_2N)CHO···HOCl	9.35	8.39	9.32
(H_2N)CHO···$HOCH_3$	6.22	6.04	6.12
(H_2N)CHO···$HONH_2$	7.02	6.82	7.07
(H_2N)CHO···HOC(O)H	12.83	11.57	12.47
(H_2N)CHO···HOC_6H_5	8.12	7.98	8.80

Table 2. Proton affinities (kcal/mol) of carbonyl oxygen of acceptor molecules at MP2/cc-pVTZ level.

Molecules	Proton affinity	Experimental
HCHO	184.65	170.40
(CN)CHO	169.09	–
(CF_3)CHO	170.62	168.00
(CH_3O)CHO	200.77	187.00
(H_2N)CHO	214.61	196.50

The change in bond lengths and stretching frequencies of O-$H_{(HB\ donor)}$ and C-$H_{(HB\ acceptor)}$ donors are reported in the table 3. The elongation of the C=O group of RCHO HB acceptor (table S22) and O-H group of R'OH HB donor is seen in all the complexes. These changes are also reflected in red shift of stretching frequencies of these bonds[14] and the largest elongation is observed for the complex HCHO···HOC(O)H for $\Delta r = 0.020$ Å. Similarly, for –CN, $–CF_3$, $–OCH_3$ and $–NH_2$ substituted RCHO complexes, C=O bond

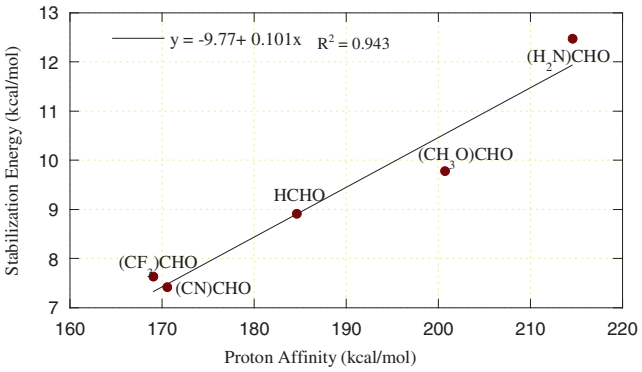

Figure 2. Variation of the stabilization energy of the RCHO···HOC(O)H complexes versus proton affinity (298 K) of the HB acceptor at MP2/cc-pVTZ level.

elongates by 0.008, 0.008, 0.024 and 0.026 Å respectively in case of HOC(O)H HB donor. Consistent with bond elongation of C=O group, the stretching frequency is red shifted and the values, $\Delta\upsilon$ range between 12.57 to 94.68 cm^{-1} (table S22). The red shift of C=O stretching frequencies has also been reported by Takei *et al.* in their DFT study on hydrogen bonded carboxylic acid···H-OR complexes.[90] For example, when acetic acid accepts a proton from water or ethanol, its C=O bond length was lengthened by 0.007 Å and the shift of frequency was by -27 cm^{-1} from the free acetic acid. As stated above that upon complex formation, the O-H bond of the HB donor is also elongated in nearly all the complexes under study and thus the HB formation accompanying a red shift in the stretching frequencies of the HB donor for the O-H bond. The O-H bond is lengthened by 0.002–0.029 Å which is more prominent in the complexes of HOCl and HOC(O)H as HB donors. The longest elongations has been indicated for the (H_2N)CHO···HOR′ complexes whereas smallest is observed in the (CN)CHO···HOR′ and CF_3CHO···HOR′ complexes reflecting role of acceptor on the elongation of O-H bond. Thus consistent with bond elongation, O-H stretch vibration exhibit a red shift which spans over a range of 0.11–604.39 cm^{-1}; this shift is again more prominent in case of (H_2N)CHO···HOR′ complexes and least in case of (CN)CHO···HOR′. On the other hand, in cases where C-H of RCHO acts as the HB donor, the C-H bond is contracted upon complex formation and the decrease in the bond length ranges between 0.001–0.006 Å. Hence, C-H bonds displays blue shift upon complex formation which is contradictory to the O-H bonds. The stretching frequency shifts for this bond lies in the range 23.01 to 92.69 cm^{-1}. The blue shift of C-H stretching band suggesting the interaction of C-H in hydrogen bonding has been reported in several research papers.[91–93]

Table 3. Hydrogen bond distances (R, Å), hydrogen bond angles (θ, degree), atomic charges (a.u.) obtained from NBO analysis; the change in bond length (Δr, Å) and shifts of stretching frequencies (cm^{-1}) for the O-H bond of HB donor upon complex formation at MP2/cc-pVTZ level.

Complexes	R		θ		Atomic charges		Δr^*	$\Delta\nu$
HCHO···HOH	O1···H5	1.999	O1-H5-O6	149.72	$q_O(q_H)$	−0.614(0.485)	0.007	−104.8
	O6···H4	2.594	O6-H4-C2	107.10	$q_O(q_H)$	−0.944(0.117)	(−0.003)	(33.16)
HCHO···HOCl	O1···H5	1.804	O1-H5-O6	162.44	$q_O(q_H)$	−0.619(0.508)	0.013	−239.32
$HCHO\cdots HOCH_3$	O1···H5	1.970	O1-H5-O6	151.48	$q_O(q_H)$	−0.613(0.483)	0.007	−150.91
$HCHO\cdots HONH_2$	O1···H5	1.916	O1-H5-O6	166.96	$q_O(q_H)$	−0.619(0.492)	0.004	−13.9
	N7···H4	2.566	N7-H4-C2	121.41	$q_N(q_H)$	−0.512(0.127)	(−0.005)	(28.95)
HCHO···HOC(O)H	O1···H5	1.809	O1-H5-O6	176.95	$q_O(q_H)$	−0.643(0.531)	0.020	−385.26
	O8···H4	2.407	O8-H4-C2	127.87	$q_O(q_H)$	−0.721(0.095)	(−0.006)	(51.42)
$HCHO\cdots HOC_6H_5$	O1···H5	1.903	O1-H5-O6	153.72	$q_O(q_H)$	−0.622(0.506)	0.009	−186.52
(CN)CHO···HOH	O1···H6	2.191	O1-H6-O7	130.08	$q_O(q_H)$	−0.541(0.478)	0.004	−28.68
	O7···H3	2.356	O7-H3-C2	113.19	$q_O(q_H)$	−0.941(0.179)	(−0.003)	(40.84)
(CN)CHO···HOCl	O1···H6	1.910	O1-H6-O7	152.18	$q_O(q_H)$	−0.550(0.502)	0.008	−145.53
$(CN)CHO\cdots HOCH_3$	O1···H6	2.163	O1-H6-O7	132.66	$q_O(q_H)$	−0.541(0.476)	0.004	−76.15
	O7···H3	2.374	O7-H3-C2	112.72	$q_O(q_H)$	−0.773(0.178)	(−0.002)	(38.64)
$(CN)CHO\cdots HONH_2$	O1···H6	2.203	O1-H6-O7	126.53	$q_O(q_H)$	−0.544(0.460)	0.002	−0.11
	O7···H3	2.364	O7-H3-C2	112.07	$q_O(q_H)$	−0.621(0.179)	(−0.002)	39.20
(CN)CHO···HOC(O)H	O1···H6	1.844	O1-H6-O7	175.47	$q_O(q_H)$	−0.571(0.523)	0.012	−256.18
	O9···H3	2.241	O9-H3-C2	130.42	$q_O(q_H)$	−0.724(0.197)	(−0.003)	(45.46)
$(CN)CHO\cdots HOC_6H_5$	O1···H6	1.957	O1-H6-O7	174.4	$q_O(q_H)$	−0.545(0.488)	0.003	−93.36
$(CF_3)CHO\cdots HOH$	O1···H8	2.138	O1-H8-O9	135.13	$q_O(q_H)$	−0.561(0.479)	0.004	−31.73
	O9···H3	2.426	O9-H3-C2	110.77	$q_O(q_H)$	−0.941(0.153)	(−0.004)	(44.99)
$(CF_3)CHO\cdots HOCl$	O1···H8	1.888	O1-H8-O9	155.44	$q_O(q_H)$	−0.569(0.502)	0.009	−139.83
$(CF_3)CHO\cdots HOCH_3$	O1···H8	2.111	O1-H8-O9	138.50	$q_O(q_H)$	−0.561(0.476)	0.004	−77.58
	O9···H3	2.463	O9-H3-C2	109.98	$q_O(q_H)$	−0.770(0.152)	(−0.003)	(44.22)
$(CF_3)CHO\cdots HONH_2$	O1···H8	2.117	O1-H8-O9	137.04	$q_O(q_H)$	−0.565(0.461)	0.003	−3.00
	O9···H3	2.500	O9-H3-C2	108.88	$q_O(q_H)$	−0.616(0.151)	(−0.003)	43.66
$(CF_3)CHO\cdots HOC(O)H$	O1···H8	1.836	O1-H8-O9	176.02	$q_O(q_H)$	−0.589(0.523)	0.013	−246.48
	O11···H3	2.278	O11-H3-C2	128.94	$q_O(q_H)$	−0.721(0.172)	(−0.005)	(57.02)
$(CF_3)CHO\cdots HOC_6H_5$	O1···H8	1.996	O1-H8-O9	143.32	$q_O(q_H)$	−0.564(0.498)	0.008	−103.71
$(CH_3O)CHO\cdots HOH$	O1···H9	1.989	O1-H9-O10	151.47	$q_O(q_H)$	−0.715(0.487)	0.007	−117.28
$(CH_3O)CHO\cdots HOCl$	O1···H9	1.781	O1-H9-O10	174.76	$q_O(q_H)$	−0.750(0.547)	0.013	−268.84
$(CH_3O)CHO\cdots HOCH_3$	O1···H9	1.957	O1-H9-O10	152.91	$q_O(q_H)$	−0.715(0.485)	0.007	−165.17
$(CH_3O)CHO\cdots HONH_2$	O1···H9	1.961	O1-H9-O10	154.55	$q_O(q_H)$	−0.725(0.494)	0.012	−71.66
	N11···H5	2.611	N11-H5-C2	117.58	$q_N(q_H)$	−0.509(0.129)	(−0.001)	(23.01)
$(CH_3O)CHO\cdots HOC(O)H$	O1···H9	1.769	O1-H9-O10	179.25	$q_O(q_H)$	−0.760(0.559)	0.022	−420.18
	O12···H5	2.435	O12-H5-C2	125.56	$q_O(q_H)$	−0.746(0.195)	(−0.003)	(44.82)
$(CH_3O)CHO\cdots HOC_6H_5$	O1···H9	1.863	O1-H9-O10	158.61	$q_O(q_H)$	−0.724(0.509)	0.010	−201.75
$(H_2N)CHO\cdots HOH$	O1···H7	1.906	O1-H7-O8	156.38	$q_O(q_H)$	−0.734(0.493)	0.011	−179.77
$(H_2N)CHO\cdots HOCl$	O1···H7	1.713	O1-H7-O8	166.65	$q_O(q_H)$	−0.739(0.516)	0.021	−385.11
$(H_2N)CHO\cdots HOCH_3$	O1···H7	1.922	O1-H7-O8	156.49	$q_O(q_H)$	−0.734(0.492)	0.011	−227.46
$(H_2N)CHO\cdots HONH_2$	O1···H7	1.834	O1-H7-O8	169.73	$q_O(q_H)$	−0.739(0.501)	0.008	−131.2
	N9···H4	2.546	N9-H4-C2	120.59	$q_N(q_H)$	−0.516(0.130)	(−0.005)	(69.69)
$(H_2N)CHO\cdots HOC(O)H$	O1···H7	1.706	O1-H7-O8	178.65	$q_O(q_H)$	−0.763(0.539)	0.029	−604.39
	O10···H4	2.357	O10-H4-C2	128.47	$q_O(q_H)$	−0.733(0.149)	(−0.006)	(92.69)
$(H_2N)CHO\cdots HOC_6H_5$	O1···H7	1.793	O1-H7-O8	160.10	$q_O(q_H)$	−0.743(0.516)	0.016	−295.99

[#] $\Delta E_{Corr} = E_{(Complex)} - [E_{(Carbonyl\ compound)} + E_{(HB\ donor)}]$ + BSSE correction; r_{vw} (Sum of van der Waal radii) $= r_O + r_H = 2.60$ Å; $r_N + r_H = 2.74$ Å

*the values are those for the O-H bond of HB donor while those in the brackets are for C-H bonds of HB acceptor

3.3 *Nature of Interactions Stabilizing the Complexes*

3.3a *NBO Analysis*: Weinhold natural bond orbital (NBO) analysis[94] has been used to quantitatively estimate the second order interaction energy ($E^{(2)} = -2$ F$ij/\Delta E ij$) due to second order interaction arising from the orbital interactions where $\Delta Eij = Ei - Ej$ is the energy difference between the interacting molecular orbitals i and j, and Fij is the Fock matrix element for the interaction between i and j orbitals. Atomic charges

Table 4. Second order delocalization energies $E^{(2)}$ in kcal/mol associated with orbital interactions and amount of charge transfer (in e) in the complexes of carbonyl compounds with HB donors at MP2/cc-pVTZ theoretical level using NBO analysis.

Complexes	Orbital interactions	$E^{(2)}$	CT (e)
HCHO···HOH	$n_{O1} \rightarrow \sigma^*_{H5\text{-}O6}$	5.19	0.007
	$n_{O6} \rightarrow \sigma^*_{C2\text{-}H4}$	0.25	
HCHO···HOCl	$n_{O1} \rightarrow \sigma^*_{H5\text{-}O6}$	14.68	0.021
$HCHO\cdots HOCH_3$	$n_{O1} \rightarrow \sigma^*_{H5\text{-}O6}$	5.99	0.010
$HCHO\cdots HONH_2$	$n_{O1} \rightarrow \sigma^*_{H5\text{-}O6}$	8.67	0.011
	$n_{N7} \rightarrow \sigma^*_{C2\text{-}H4}$	0.89	
HCHO···HOC(O)H	$n_{O1} \rightarrow \sigma^*_{H5\text{-}O6}$	17.23	0.022
	$n_{O8} \rightarrow \sigma^*_{C2\text{-}H4}$	0.88	
$HCHO\cdots HOC_6H_5$	$n_{O1} \rightarrow \sigma^*_{H5\text{-}O6}$	7.57	0.015
(CN)CHO···HOH	$n_{O1} \rightarrow \sigma^*_{H6\text{-}O7}$	1.44	0.001
	$n_{O7} \rightarrow \sigma^*_{C2\text{-}H3}$	0.61	
(CN)CHO···HOCl	$n_{O1} \rightarrow \sigma^*_{H6\text{-}O7}$	7.95	0.011
$(CN)CHO\cdots HOCH_3$	$n_{O1} \rightarrow \sigma^*_{H6\text{-}O7}$	1.66	0.002
	$n_{O7} \rightarrow \sigma^*_{C2\text{-}H3}$	0.62	
$(CN)CHO\cdots HONH_2$	$n_{O1} \rightarrow \sigma^*_{H6\text{-}O7}$	1.20	0.002
	$n_{O7} \rightarrow \sigma^*_{C2\text{-}H3}$	0.51	
(CN)CHO···HOC(O)H	$n_{O1} \rightarrow \sigma^*_{H6\text{-}O7}$	13.7	0.014
	$n_{O9} \rightarrow \sigma^*_{C2\text{-}H3}$	1.80	
$(CN)CHO\cdots HOC_6H_5$	$n_{O1} \rightarrow \sigma^*_{H6\text{-}O7}$	6.87	0.007
$(CF_3)CHO\cdots HOH$	$n_{O1} \rightarrow \sigma^*_{H8\text{-}O9}$	2.06	0.003
	$n_{O9} \rightarrow \sigma^*_{C2\text{-}H3}$	0.51	
$(CF_3)CHO\cdots HOCl$	$n_{O1} \rightarrow \sigma^*_{H8\text{-}O9}$	8.96	0.008
$(CF_3)CHO\cdots HOCH_3$	$n_{O1} \rightarrow \sigma^*_{H8\text{-}O9}$	2.39	0.002
	$n_{O9} \rightarrow \sigma^*_{C2\text{-}H3}$	0.48	
$(CF_3)CHO\cdots HONH_2$	$n_{O1} \rightarrow \sigma^*_{H8\text{-}O9}$	2.31	0.002
	$n_{O9} \rightarrow \sigma^*_{C2\text{-}H3}$	0.38	
$(CF_3)CHO\cdots HOC(O)H$	$n_{O1} \rightarrow \sigma^*_{H8\text{-}O9}$	14.21	0.017
	$n_{O11} \rightarrow \sigma^*_{C2\text{-}H3}$	1.63	
$(CF_3)CHO\cdots HOC_6H_5$	$n_{O1} \rightarrow \sigma^*_{H8\text{-}O9}$	5.12	0.008
$(CH_3O)CHO\cdots HOH$	$n_{O1} \rightarrow \sigma^*_{H9\text{-}O10}$	5.64	0.008
$(CH_3O)CHO\cdots HOCl$	$n_{O1} \rightarrow \sigma^*_{H9\text{-}O10}$	16.55	0.020
$(CH_3O)CHO\cdots HOCH_3$	$n_{O1} \rightarrow \sigma^*_{H9\text{-}O10}$	6.57	0.010
$(CH_3O)CHO\cdots HONH_2$	$n_{O1} \rightarrow \sigma^*_{H9\text{-}O10}$	6.98	0.007
	$n_{N11} \rightarrow \sigma^*_{C2\text{-}H5}$	0.65	
$(CH_3O)CHO\cdots HOC(O)H$	$n_{O1} \rightarrow \sigma^*_{H9\text{-}O10}$	20.58	0.025
	$n_{O12} \rightarrow \sigma^*_{C2\text{-}H5}$	0.81	
$(CH_3O)CHO\cdots HOC_6H_5$	$n_{O1} \rightarrow \sigma^*_{H9\text{-}O10}$	11.94	0.017
$(H_2N)CHO\cdots HOH$	$n_{O1} \rightarrow \sigma^*_{H7\text{-}O8}$	8.84	0.013
$(H_2N)CHO\cdots HOCl$	$n_{O1} \rightarrow \sigma^*_{H7\text{-}O8}$	23.53	0.046
$(H_2N)CHO\cdots HOCH_3$	$n_{O1} \rightarrow \sigma^*_{H7\text{-}O8}$	10.23	0.015
$(H_2N)CHO\cdots HONH_2$	$n_{O1} \rightarrow \sigma^*_{H7\text{-}O8}$	13.49	0.017
	$n_{N9} \rightarrow \sigma^*_{C2\text{-}H4}$	0.96	
$(H_2N)CHO\cdots HOC(O)H$	$n_{O1} \rightarrow \sigma^*_{H7\text{-}O8}$	28.33	0.047
	$n_{O10} \rightarrow \sigma^*_{C2\text{-}H4}$	1.14	
$(H_2N)CHO\cdots HOC_6H_5$	$n_{O1} \rightarrow \sigma^*_{H7\text{-}O8}$	17.07	0.023

derived from the NBO analysis reflect the relative importance of electrostatic interactions associated with the complexes while the extent of charge transfer is suggested by $E^{(2)}$ values, the second order stabilization energies associated with orbital interactions between the lone pair of the HB acceptor and molecular orbital of the HB donor group. The values of atomic charges

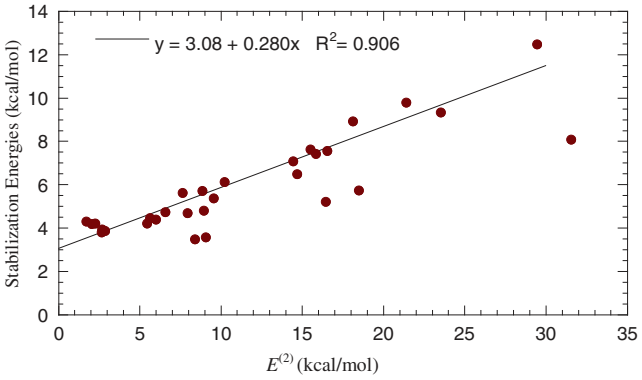

Figure 3. A plot of the stabilization energies of the complexes versus second order delocalization energies obtained from NBO analysis at MP2/cc-pVTZ level.

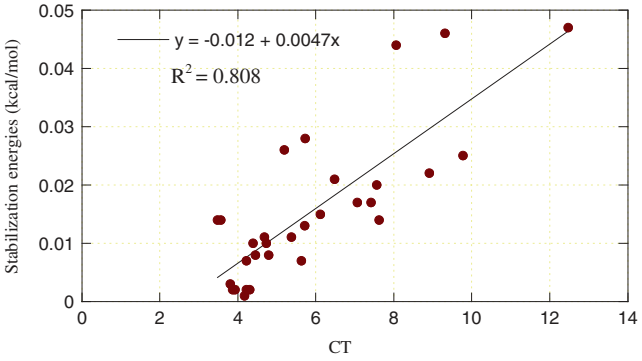

Figure 4. Correlation of the charge transfer between monomers versus stabilization energies of the complexes at MP2/cc-pVTZ level.

of the HB acceptor (oxygen) and HB donor (hydrogen) evaluated at MP2/cc-pVTZ level employing NBO analysis are listed in table 3. The atomic charge analysis indicates that the hydrogen atoms of the HB donors HOR′ have atomic charge in the range +0.483 to +0.531 while the O of HCHO molecules as the HB acceptor has atomic charge in the range of −0.614 to −0.643 unit suggesting strong electrostatic interactions. It is also evident that the electron charge density on the oxygen atom of RCHO molecule increases in case of $–OCH_3$ and $–NH_2$ substituted complexes in comparison to –CN and $–CF_3$ substituted complexes, thereby suggesting stronger electrostatic interactions in the former case than latter. Within the complexes involving unconventional HB donor group e.g., C-H group of RCHO as the HB donor in some complexes, the atomic charge on hydrogen is comparatively lower but the electrostatic contribution remains significant because of high electron density present at the O or N of the HB acceptor HOR′. The loss of electron density on hydrogen atom involved in the hydrogen bonding is accepted as the phenomenon accompanying HB formation. The atomic charges in table 3 also suggest the hydrogen nuclei are

deshielded upon HB formation. In addition the charge density on oxygen atom of RCHO acting as HB acceptor is increased. Both the variations favor the electrostatic attractions for the HB. Only small variations in atomic charges of other atoms upon aggregation are seen.

The formation of RCHO···HOR′ bond is accompanied by the charge transfer from the lone pair of the HB accepting oxygen atom of RCHO to the σ^* orbital of the H-O covalent bond of HOR′. The leading orbital interactions and the respective $E^{(2)}$ values for the complexes under study have been given in table 4. It is evident from the table that some of the complexes are also stabilized by additional HBs which is supported by the electron delocalization from the HB acceptor to donor in the orbital interactions. The NBO analysis indicates that the orbital interactions in the complexes under study for $n_{O1(carbonyl)} \rightarrow \sigma^*_{H-O(HB\ donor)}$ are stronger in comparison to that for the second HB if present. The second order stabilization energies ($E^{(2)}$ values) indicate that the charge transfer is relatively weaker in the complexes of (CN)CHO and (CF_3)CHO and stronger in the complexes of (CH_3O)CHO and (H_2N)CHO than those of HCHO, again suggesting that the HB acceptor ability of the carbonyl group is lowered by presence of –CN and –CF_3 substituents and enhanced with –OCH_3 and –NH_2 substituents. The highest $E^{(2)}$ values has been obtained for the complexes RCHO···HOC(O)H which is consistent with the earlier results in this work. The NBO analysis of HOC(O)H monomeric unit suggests electron delocalization involving lone pairs/π electrons in conjugation with the C=O π bond (table S23 in supplementary information). With complex formation marginal to small variations in the electron delocalizations appear with few exceptions that play important role. As in case of the complexes of HOC(O)H, the orbital interactions $n_{O(of\ OH)} \rightarrow \pi^*_{C-O}$ are strengthened, thereby suggesting that the C=O···H-O-R′ HB is supported by resonance. The HBs involving –OH of HOC_6H_5 form another resonance assisted hydrogen bonded set of complexes. The electron donor ability of carbonyl oxygen in case of (H_2N)CHO is

Table 5. SAPT components (kcal/mol) of the Interaction Energies for the complexes of carbonyl compounds with HB donors under study at MP2/cc-pVTZ level.

Complexes	E_{els}	E_{ind}	E_{disp}	E_{exc}	$\delta E^{HF}_{int,r}$	E_{int}
HCHO···HOH	−8.31	−3.19	−2.28	9.88	−0.72	−4.62
HCHO···HOCl	−10.84	−5.97	−3.20	15.66	−1.53	−5.88
HCHO···$HOCH_3$	−8.33	−3.40	−2.82	10.57	−0.76	−4.74
HCHO···$HONH_2$	−10.12	−4.54	−3.28	13.92	−1.15	−5.17
HCHO···HOC(O)H	−15.11	−8.42	−4.51	21.81	−2.31	−6.23
HCHO···HOC_6H_5	−10.21	−5.56	−2.82	14.69	−1.31	−5.21
(CN)CHO···HOH	−7.55	−2.20	−2.16	7.60	−0.41	−4.70
(CN)CHO···HOCl	−8.94	−4.41	−3.09	12.29	−0.88	−5.03
(CN)CHO···$HOCH_3$	−7.68	−2.39	−2.50	8.17	−0.47	−4.87
(CN)CHO···$HONH_2$	−7.47	−2.27	−2.39	7.55	−0.42	−4.99
(CN)CHO···HOC(O)H	−13.32	−7.12	−4.42	18.86	−1.80	−7.81
(CN)CHO···HOC_6H_5	−8.80	−4.31	−3.02	11.98	−0.86	−5.01
(CF_3)CHO···HOH	−7.09	−2.04	−2.08	7.15	−0.38	−4.44
(CF_3)CHO···HOCl	−7.62	−4.11	−2.85	11.34	−0.93	−4.17
(CF_3)CHO···$HOCH_3$	−7.25	−2.20	−2.41	7.69	−0.42	−4.60
(CF_3)CHO···$HONH_2$	−7.10	−2.17	−2.33	7.30	−0.40	−4.69
(CF_3)CHO···HOC(O)H	−9.75	−6.31	−4.30	15.69	−1.61	−6.28
(CF_3)CHO···HOC_6H_5	−7.40	−2.18	−2.28	7.60	−0.48	−4.74
(CH_3O)CHO···HOH	−8.84	−3.45	−2.48	10.61	−0.74	−4.90
(CH_3O)CHO···HOCl	−11.81	−6.23	−3.48	16.16	−1.67	−7.04
(CH_3O)CHO···$HOCH_3$	−9.01	−3.83	−2.90	11.71	−0.82	−4.85
(CH_3O)CHO···$HONH_2$	−10.00	−4.76	−3.00	13.42	−1.03	−5.36
(CH_3O)CHO···HOC(O)H	−16.70	−9.38	−5.00	24.17	−2.58	−9.49
(CH_3O)CHO···HOC_6H_5	−10.11	−4.72	−3.05	13.56	−1.14	−5.46
(H_2N)CHO···HOH	−11.11	−4.69	−2.88	13.58	−1.10	−6.21
(H_2N)CHO···HOCl	−15.84	−8.99	−4.08	21.64	−2.46	−9.74
(H_2N)CHO···$HOCH_3$	−11.25	−5.20	−3.65	14.94	−1.20	−6.36
(H_2N)CHO···$HONH_2$	−13.20	−6.29	−4.10	18.19	−1.64	−7.04
(H_2N)CHO···HOC(O)H	−21.07	−12.29	−5.87	30.58	−3.59	−12.25
(H_2N)CHO···HOC_6H_5	−13.89	−6.30	−4.19	19.09	−1.85	−7.14

enhanced because of $–NH_2$ substituent which is apparent from the $n_N \rightarrow \sigma^*_{O1\text{-}C2}$ orbital interactions which are further increased on complex formation with different molecules under study. Figure 3 shows a good linear relationship between the stabilization energies and $E^{(2)}$ values with $R^2 = 0.906$.

The net charge transfer (CT) from the HB acceptor to the HB donor has been evaluated utilizing the computed natural charges and the values are reported in same table. The positive value of the CT upon the formation of complex indicates the charge flow from the carbonyl compound to the hydroxyl molecule. It should be noted that the amount of CT in the complexes studied here increases in the order $(CF_3)CHO < (CN)CHO < HCHO < (CH_3O)CHO < (H_2N)CHO$ for the HB acceptors. For the NPA charges of the complexes, a plot of CT versus stabilization energy at MP2/cc-pVTZ (figure 4) yields a linear relationship ($R^2 = 0.808$). The low correlation is understandable as the two HBs presents in many of the complexes transfer charge in both directions. Thus, from NBO analysis, it also is evident that the HB acceptors that are more basic i.e.

Table 6. Summary of AIM parameters (a.u.) in the complexes of carbonyl compounds with HB donors at MP2/cc-pVTZ level.

Complexes	$\rho_{A\ldots D}$	$\nabla^2_{\rho A\ldots D}$	Complexes	$\rho_{A\ldots D}$	$\nabla^2_{\rho A\ldots D}$
HCHO···HOH			(CF_3)CHO···HONH$_2$		
O1···H5	0.021	0.084	O1···H8	0.017	0.072
			O9···H3	0.009	0.040
HCHO···HOCl			(CF_3)CHO···HOC(O)H		
O1···H5	0.039	0.104	O1···H8	0.030	0.096
			O11···H3	0.013	0.056
HCHO···HOCH$_3$			(CF_3)CHO···HOC$_6$H$_5$		
O1···H5	0.023	0.088	O1···H8	0.021	0.088
HCHO···HONH$_2$			(CH_3O)CHO···HOH		
O1···H5	0.025	0.088	O1···H9	0.022	0.084
N7···H4	0.010	0.036			
HCHO···HOC(O)H			(CH_3O)CHO···HOCl		
O1···H5	0.033	0.096	O1···H9	0.035	0.104
O8···H4	0.010	0.040			
HCHO···HOC$_6$H$_5$			(CH_3O)CHO···HOCH$_3$		
O1···H5	0.027	0.096	O1···H9	0.024	0.092
(CN)CHO···HOH			(CH_3O)CHO···HONH$_2$		
O1···H6	0.014	0.064	O1···H9	0.023	0.076
O7···H3	0.011	0.052	N11···H5	0.012	0.044
(CN)CHO···HOCl			(CH_3O)CHO···HOC(O)H		
O1···H6	0.028	0.096	O1···H9	0.036	0.100
			O12···H5	0.010	0.040
(CN)CHO···HOCH$_3$			(CH_3O)CHO···HOC$_6$H$_5$		
O1···H6	0.015	0.068	O1···H9	0.029	0.100
O7···H3	0.011	0.052			
(CN)CHO···HONH$_2$			(H_2N)CHO···HOH		
O1···H6	0.014	0.064	O1···H7	0.027	0.096
O7···H3	0.011	0.052			
(CN)CHO···HOC(O)H			(H_2N)CHO···HOCl		
O1···H6	0.030	0.092	O1···H7	0.043	0.112
O9···H3	0.014	0.060			
(CN)CHO···HOC$_6$H$_5$			(H_2N)CHO···HOCH$_3$		
O1···H6	0.021	0.084	O1···H7	0.029	0.100
(CF_3)CHO···HOH			(H_2N)CHO···HONH$_2$		
O1···H8	0.015	0.072	O1···H7	0.031	0.100
O9···H3	0.010	0.048	N9···H4	0.010	0.036
(CF_3)CHO···HOCl			(H_2N)CHO···HOC(O)H		
O1···H8	0.028	0.096	O1···H7	0.043	0.108
			O10···H4	0.011	0.048
(CF_3)CHO···HOCH$_3$			(H_2N)CHO···HOC$_6$H$_5$		
O1···H8	0.017	0.072	O1···H7	0.035	0.108
O9···H3	0.010	0.044			

having $-OCH_3$ and $-NH_2$ substituents on the carbonyl leads to higher values of CT than those with –H, –CN and $-CF_3$ substituents.

3.3b *SAPT Analysis*: Decomposition of the stabilization energy by means of SAPT (symmetry adapted perturbation theory) method also offers a valuable clues about the nature of the interaction stabilizing the complexes.[25] The method decomposes the stabilization energy arising from the intermolecular interactions into several components like electrostatic, induced and dispersion interactions etc. In this paper, the individual energy components E_{els}, E_{ind}, E_{disp} and E_{exch} were evaluated employing the SAPT procedures at MP/cc-pVTZ basis set. The components of SAPT are collected in table 5. As can be seen from the table that the E_{exch} term is destabilizing, and the E_{els}, E_{ind} and E_{disp} terms are stabilizing. The E_{exch} term arise mainly from the antisymmetry requirement of the wave function and the large magnitude of this term is the result of shorter binding distance. It can be observed from the table that the most important stabilizing component is electrostatic, which corresponds between 53 and 60% of the total attraction terms in case of HCHO complexes. The second most important attraction term is E_{ind}; while the E_{disp} term is playing least role in stability of the complexes. On the other hand, in case of –CN and $-CF_3$ substituted complexes, the electrostatic interactions (E_{els}) contribute 52–64% and 47–63% of the total attractive forces respectively, dominating over other two stabilizing terms. But the percentage contribution of the E_{ind} (18–28% & 18–30%) and E_{disp} (18–20% & 18–21%) terms for above cases suggests the relative importance of the E_{ind} term over the E_{disp} term. It is interesting to note that for the complexes of (CN)CHO and (CF_3)CHO HB acceptors with $HOCH_3$ and $HONH_2$ HB donors, the percentage contribution of the E_{disp} term is little higher than the E_{ind} term, reflecting the effect of substituents on both the HB donor and acceptor. In case of (CH_3O)CHO complexes, the percentage contribution of the E_{els}, E_{ind} and E_{disp} terms to the total attraction terms are 53–59%, 23–30% and 16–19% respectively, thus indicating the relative importance of all the terms. Similarly, the complexes of (H_2N)CHO reveal that the highest contribution is from the electrostatic forces. The complexes of the selected carbonyl compounds with HOC(O)H HB donor have the E_{els} component 47–54% to the total attractive interactions while the E_{ind} component falls in the range 28–32%.

3.3c *AIM Analysis*: The theory of atoms in molecules (AIM) has offered a valuable tool to understand the concept of a HB.[78–80] AIM theory takes electron density ρ as a starting point. The topology of electron density is generally used to determine the existence and the strength of HB qualitatively. The interaction between any two atoms in the system is characterized by the parameters associated with the electron density at the bond critical point (bcp) known as (3,-1) critical point. ∇^2_ρ indicates whether the electron density is locally concentrated ($\nabla^2_\rho < 0$) or depleted ($\nabla^2_\rho > 0$). The values of topological properties at the bcp characterizing the HBs are reported in table 6. The ∇^2_ρ values are clearly positive, as expected for the HB; hence reflecting the closed-shell type of interaction. As can be seen in the table, the complexes satisfy the Popelier's criteria[95] for existence of a HB with values of ρ and ∇^2_ρ well within the listed ranges in most of the cases. The ρ values at the bcp for the C=O···H-O bonds decreases with presence of –CN and $-CF_3$ substituents, whereas the values increase with $-OCH_3$ and $-NH_2$ substituents on the carbonyl carbon. The additional weak HBs wherein C-H of carbonyl molecules acting as the HB donor have lower values of ρ and ∇^2_ρ at the bcp. It is well documented that the electron densities and their laplacian at the bcps correlate with the interaction energies. The relationship between the electron density at the bcps and the stabilization energies for the hydrogen bonded complexes have been established at MP2/cc-pVTZ level. As illustrated in figure 5, there exists a linear relationship between the stabilization energies and ρ values and the correlation coefficient, R^2 is as high as 0.870. The lower correlation coefficient is the result of multiple interactions present in the complexes.

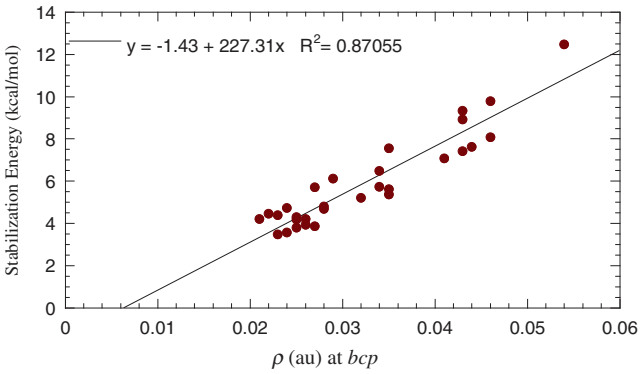

Figure 5. Relationship of the stabilization energies of the complexes and electron density ρ (au) at the bcp at MP2/cc-pVTZ level.

3.4 *Analysis Based on Molecular electrostatic potential (MESP)*

The molecular electrostatic potential (MESP) is also a powerful tool for description of strength of HB. The

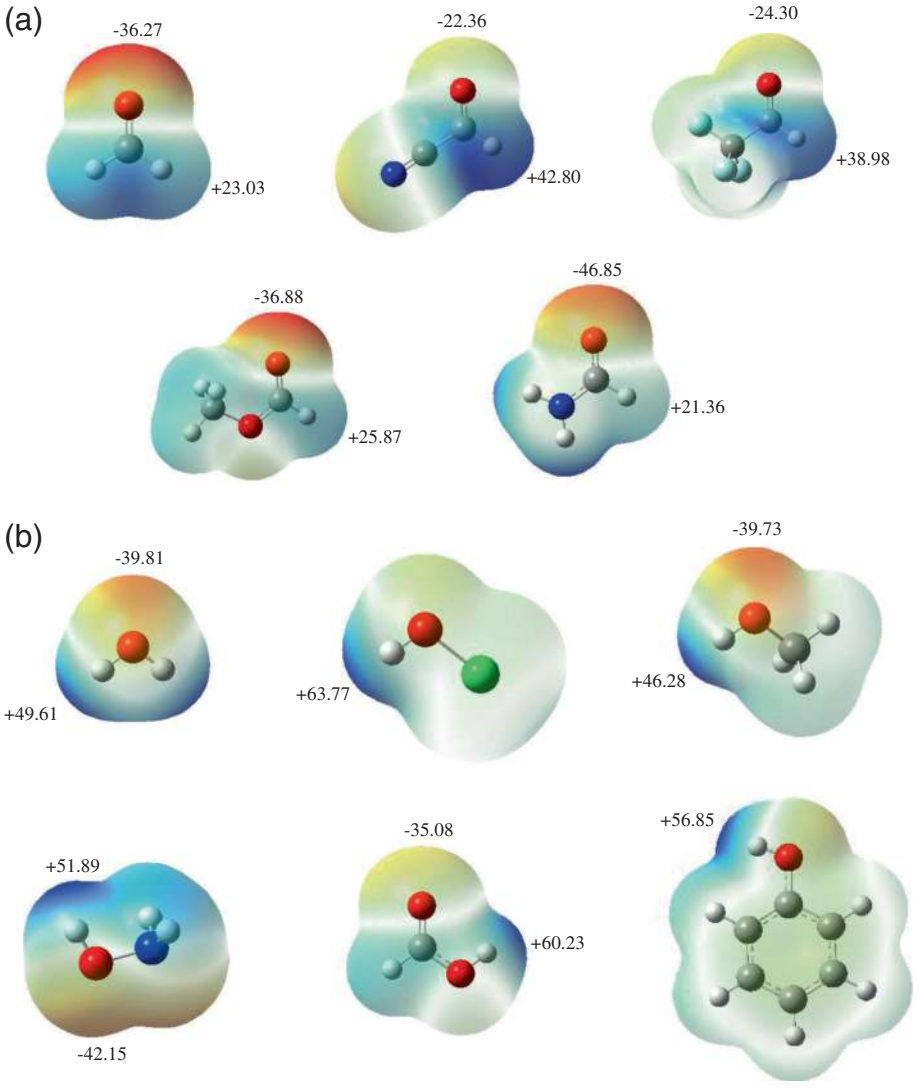

Figure 6. (a) Molecular electrostatic potential (in kcal/mol) of the RCHO (R = H, CN, CF_3, OCH_3, NH_2) acceptors at MP2/cc-pVTZ level. (b) Molecular electrostatic potential (in kcal/mol) of the HOR′(R′ = H, Cl, CH_3, NH_2, C(O)H, C_6H_5) donors at MP2/cc-pVTZ level.

V_{min}, most negative valued MESP point of the HB acceptor and the V_{max} most positive valued MESP point of the HB donor predict the sites and directionality of the HBs in variety of complexes. We have reinforced our analysis of O···H interactions in investigated model molecules by viewing MESP on the electron density isosurfaces of 0.001 au as suggested by Bader *et al.*[96] The MESP surfaces of the HB acceptor molecules, RCHO (R = H, CN, CF_3, OCH_3, NH_2) and donor HOR′ (R′ = H, Cl, CH_3, NH_2, C(O)H, C_6H_5) molecules are represented in the figures 6a and 6b respectively. The MESP clearly indicates that an area of electrostatic potential minima (red to yellow region) V_{min}, on the acceptor molecules points binds to the positive area (blue region) on the donor molecules. The values of electrostatic potential for the atoms forming HB are shown along with the figures. It can be observed that there is progressive increase in electrostatic potential minima, V_{min} on the carbonyl oxygen in the order (CN)CHO < (CF_3)CHO < HCHO < (CH_3O)CHO < (H_2N)CHO and for the electrostatic potential maxima, V_{max} on the HB donors the order is $HOCH_3$ < HOH < $HONH_2$ < HOC_6H_5 < HOC(O)H < HOCl. As already pointed out from the analysis so far that HOR′ also acts as the HB acceptor towards RCHO molecule, thus the negative potential on the oxygen atom of HOR′ is also displayed in the figure. A good correlation (R^2 = 0.912) between the electrostatic potential minima V_{min} on the carbonyl oxygen of the RCHO acceptor and the stabilization energies of the RCHO···HOC(O)H (i.e. with same HB donor) complexes has been obtained as displayed in figure 7.

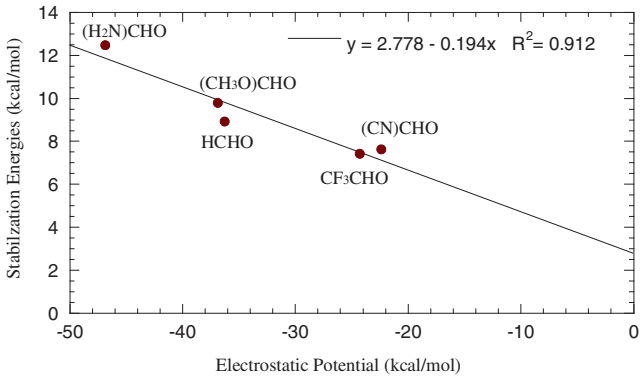

Figure 7. Relationship of the stabilization energies of the RCHO··· HOC(O)H complexes with electrostatic potential of the HB acceptors at MP2/cc-pVTZ level.

4. Conclusions

The present study analyzes the effect of presence of substituents both at the HB acceptor i.e., RCHO and HB donor i.e. HOR′ on the strength of RCHO···HOR′ complexes at the MP2/cc-pVTZ level. Among the various substituents present at the RCHO, they can be divided into two types - the electron donating group, EDG (–OCH_3 and –NH_2), and the electron withdrawing group, EWG (–CN and –CF_3) and their comparison is made relative to unsubstituted one i.e., HCHO complexes. It is found that the EDG substituents increase the HB strength while the EWG decrease the same with respect to HCHO. The –NH_2 being the strongest EDG exhibit highest strength of the HB; on the other hand –CN being a EWG has lowest strength among all the complexes under study. Similarly, the effect of different substituents at the O-H donor group of HOR′ has also been studied and it is seen that all the substituents enhance the HB strength relative to HOH as reference, strongest one is the –C(O)H while –CH_3 enhance stabilization energy to a least extent. The NBO, SAPT, AIM and MESP analysis are applied to analyze the nature of interactions stabilizing the complexes and the above results are supported by these latter methods. The SAPT suggest that the electrostatic interactions dominate over the inductive and dispersive ones. NBO analysis however, infers that there is strong charge transfer from the HB acceptor to donor and its contribution is larger in the strongly bound complexes. The results are supported by the change in stretching frequency shifts of the HB donor groups. Red shift is encountered in the O-H bond as the HB donor while blue shift in the C-H bond is reflected upon complex formation. The most strongly bound complexes of type RCHO···HOC(O)H has resonance assisted hydrogen bonding interactions as the conjugative interactions involving lone pair of electrons at the hydroxyl oxygen with carbonyl favors the charge acceptor ability of σ^*_{O-H} bond.

Supplementary Information

The optimized parameters for the HB acceptors (RCHO) and donors (HOR′) are given in the tables S1-S6 at B3LYP/6-31++G** (L1), MP2/6-31++G** (L2) and MP2/cc-pVTZ (L3) theoretical levels. Their hydrogen bonded complexes RCHO···HOR′ (R = H, CN, CF_3, OCH_3, NH_2; R′ = H, Cl, CH_3, NH_2, HC=O and C_6H_5) at the above mentioned levels are included in the tables S7-S21. The change in C=O bond length for the RCHO HB acceptors upon complex formation at MP2/cc-pVTZ level are included in table S22. Table S23 lists the second order stabilization energies ($E^{(2)}$) for the monomer HOC(O)H and its respective complexes with RCHO acceptors signifying resonance assisted HBs at MP2/cc-pVTZ level. Supplementary Information is available at www.ias.ac.in/chemsci.

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