



Molecular electrostatic potential analysis of non-covalent complexes

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Abstract. *Ab initio* MP4/Aug-cc-pvDZ//MP2/6-311++g(d,p) level interaction energy (E_{int}) and molecular electrostatic potential analysis (MESP) of a large variety of non-covalent intermolecular complexes, viz. tetrel, chalcogen, pnictogen, halogen, hydrogen, dihydrogen and lithium bonded complexes have been reported. The electronic changes associated with the non-covalent complex formation is monitored in terms of MESP minimum (V_{min}) in the free and complexed states of the donor and acceptor molecules as well as in terms of MESP at the donor and acceptor atoms (V_n) of the free monomers and complexes. The change in V_{min} or V_n on the donor molecule ($\Delta V_{\text{min}}(\text{D})$ or $\Delta V_n(\text{D})$) during complex formation is proportional to its electron donating ability while such a change on the acceptor molecule ($\Delta V_{\text{min}}(\text{A})$ or $\Delta V_n(\text{A})$) is proportional to its electron accepting ability. Further, the quantities $\Delta\Delta V_{\text{min}} = \Delta V_{\text{min}}(\text{D}) - \Delta V_{\text{min}}(\text{A})$ and $\Delta\Delta V_n = \Delta V_n(\text{D}) - \Delta V_n(\text{A})$ have shown strong linear correlations with E_{int} of the complex (E_{int} values fall in the range 0.7 to 46.2 kcal/mol for 54 complexes) and suggest that the intermolecular non-covalent interactions in a wide variety of systems can be monitored and assessed in terms of change in MESP due to complex formation in the gas phase. With the incorporation of solvent effect in the calculation, charged systems showed significant deviations from the linear correlation. The MESP based analysis proposes that the large variety of intermolecular non-covalent complexes considered in this study can be grouped under the general category of electron donor-acceptor (eDA) complexes.

Keywords. Non-covalent complex; hydrogen bond; halogen bond; dihydrogen bond; pnictogen bond; tetrel bond; lithium bond; chalcogen bond; molecular electrostatic potential.

1. Introduction

Non-covalent interactions between molecules, which span a wide range of strength from weak van der Waals interactions between non-polar entities to ion-ion interactions that can be very strong, play a key role in crystal engineering, molecular recognition and controls the structures adopted by molecules and their transition from one conformer to other.^{1–6} These interactions include hydrogen (HB),^{4,7–9} dihydrogen (DHB),^{10–12} halogen (XB),^{13–19} pnictogen (PB),^{20–22} chalcogen (CB),^{23–28} tetrel (TB),^{29–33} and lithium (LiB)^{34–36} bond. Among them, the most extensively studied one is hydrogen bonding interaction. The conventional HBs, where the proton donor and acceptor atoms are electronegative atoms like N, O and F, have been generalized in recent researches in directions such as the C, a less electronegative atom than the conventional proton donor, can act as proton donor

and the hydrogen bond acceptors can donate electron density *via* π bonds, σ bonds, metal atoms and even another hydrogen atom rather than the conventional lone pairs.^{37,38}

Many theoretical models have been developed to account the features of hydrogen bond. Gilli and co-workers proposed the electrostatic-covalent model of hydrogen bonding. According to them, weak hydrogen bonds are electrostatic in nature and become more covalent with increasing bond strength.^{39,40} Coulson divided the columbic attraction energy of hydrogen bond into four factors: electrostatic, covalent, and repulsive and dispersion contributions.⁴¹ Pimentel and McClellan introduced the MO model for hydrogen bonding.⁴² They suggested that hydrogen bonds can be considered as three-centre four-electron bonds. Crabtree and co-workers introduced the term dihydrogen bond which describes the interaction of the type X-H \cdots H-Y, where X is more electronegative than hydrogen and Y, usually transition metals or boron atom, is less electronegative than hydrogen.^{43,44} LiB interactions designated as X...Li-Y, where X is a species with a region of high electron density, is a counter part to the HB

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and have properties somewhat similar to HB.⁴⁵ As Li is more electropositive than hydrogen, Li-Y bond will be more ionic compared to H-Y bond and therefore LiB bonds appear stronger than HB.

The interactions XB, TB, CB and PB can be classified as “ σ -hole bonds” proposed by Politzer and Murray.^{13,46,47} The term “ σ -hole” usually refers to an empty outer lobe of a p orbital involved in forming a covalent bond, especially when one of the atoms is highly electronegative, that corresponds to a positive region of the molecular electrostatic potential (MESP) and can act as an electron-pair acceptor in non-covalent interactions. Tetrel, pnictogen, chalcogen and halogen bonds, where the elements respectively are from group 14 to 17 acting as electron acceptors, are in some way analogous to hydrogen bonding. The positive “ σ -hole” on the outermost surface of these elements (which are σ -bonded to usually highly electronegative atoms) interacts with negative sites on the other molecules. These interactions are directional due to the localization of the electron acceptor site (σ -hole) on the extension of the covalent bond.⁴⁸

MESP which can be calculated from theoretically derived electron density or measured experimentally has been proven useful in understanding the interactive behaviour and properties of molecules.⁴⁹⁻⁶⁰ The most negative-valued points in the MESP topography, usually indicated with the notation V_{\min} is widely used to gauge the electron donating properties of a molecule.⁶¹ Similarly, MESP at a nucleus, referred to as V_n is also used as a parameter to measure the interactive behaviour of a molecule with respect to a particular atom towards the electron rich/electron deficient site of another molecule.^{50,51} Since V_n measures MESP at the position of atom A due to the rest of the nuclei and all the electrons, its interactions with other chemical entities are accurately reflected on changes in V_n values.⁵⁴ In a recent study based on MESP analysis, Mohan and Suresh have suggested that the definition of electron donor-acceptor (eDA) interaction holds good for the hydrogen (HB), halogen (XB) and dihydrogen bonded (DHB) non-covalent dimers.⁶¹ They used MESP features to quantify the donating power of the electron donating atom as well as the accepting power of the electron accepting atom (usually the H atom). Further, they reported a strong linear correlation between a MESP based parameter $\Delta\Delta V_n$ (difference of the change of MESP at nuclei of donor and acceptor atoms due to complex formation) and interaction energy, E_{int} for a large variety of the non-covalent dimers in the categories HB, DHB, and XB. The MESP based eDA concept proposed by Mohan and Suresh has unified the HB, DHB, and XB non-covalent

complexes in a single category, the eDA complex.⁶¹ In the present work, the $\Delta\Delta V_n$ versus E_{int} correlation has been analysed for a large variety of non-covalent complexes including the hitherto unexplored CB, TB, PB and LiB complexes. This work will show that eDA concept is applicable for all these systems.

2. Computational Methods

The complexes selected for this study include hydrogen (HB), dihydrogen (DHB), halogen (XB), chalcogen (CB), pnictogen (PB), tetrel (TB) and lithium (LiB) bonded dimers. The optimization of the geometry of all these systems (six examples from each category) and their vibrational frequency analysis have been done at MP2/6-311++G(d,p) level of theory. All the structures correspond to minima on the potential energy surface. Single point energy calculation using MP4/Aug-cc-pvDZ level of theory is performed on MP2/6-311++G(d,p) level optimized structures to obtain more accurate energy values. Moreover, the counterpoise procedure of Boys and Bernardi⁶² has been used at MP4/Aug-cc-pvDZ level to obtain the basis set superposition error (BSSE). The BSSE-corrected binding energy (E_{int}) of the complexes is calculated as the difference between the energy of the complexes and their constituent monomers.

Molecular electrostatic potential (MESP) arise due to the static charge distribution of the molecule which at any point in the space with position vector \mathbf{r} can be calculated using the equation,

$$V(\mathbf{r}) = \sum_A^N \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \quad (1)$$

where $\rho(\mathbf{r}')$ is a continuous electron density and Z_A is the charge on nucleus of atom A located at a distance \mathbf{R}_A .^{54,58} The MESP at the nucleus (V_n) of a particular atom A in the molecule positioned at \mathbf{R}_A can be defined by the equation (2) which measures the electrostatic potential at that point due to the continuous electron density and the rest of the nuclei.

$$V_n = \sum_{B \neq A} \frac{Z_B}{|\mathbf{R}_B - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \quad (2)$$

MESP properties of monomers and non-covalent dimers are calculated at MP4/Aug-cc-pvDZ//MP2/6-311++G+(d,p) level using Gaussian09⁶³ program. Both V_{\min} and V_n have been calculated for all the molecules. The effect of solvent (dichloromethane) in geometries, interaction energies and MESP properties

of a representative set of non-covalent complexes are also calculated by the SMD solvation model which is based on the quantum mechanical charge density of solute molecule interacting with a continuum description of the solvent⁶⁴ (MP4/Aug-cc-pvDZ-SMD//MP2/6-311++G+(d,p)-SMD level calculations, solvent used is dichloromethane).

3. Results and Discussion

The HB systems include the conventional systems (electron rich lone pair site of a molecule interacts with hydrogen atom on another molecule) and unconventional systems (π -bonds, σ -bonds and metal atoms act as electron donating centres to electron deficient hydrogen atom on another molecule). Positively charged HB dimers (HB^+) and negatively charged HB dimers (HB^-) are also considered. In LiB category, $\text{X}\dots\text{Li}-\text{Y}$ interaction describes the interaction between an electron rich centre X and an electropositive Li. In DHB dimers, an electron rich H center interacts with an electron deficient H center. For all other cases, *viz.* XB, CB, PB, and TB, the dimers can be grouped under one title, the σ -hole bonding interactions as portrayed by Politzer *et al.* In such cases, the electron dense region of one molecule interacts with the electron deficient region, the σ -hole of another molecule. In Table 1, the systems selected for this study arranged in nine categories, *viz.*, HB, HB^+ , HB^- , CB, PB, XB, LiB, DHB and TB are given. The electron donating and withdrawing atoms are indicated in blue and red colour, respectively, wherever possible. Unless otherwise mentioned, hereafter each example (total 54 complexes) will be named by the category name followed by a number that corresponds to the entry number given in Table 1. For example, HB1 and HB2 are $\text{HCHO}\dots\text{HF}$ and $\text{Guanine}\dots\text{HCl}$, respectively. Apart from these case studies, complexes such as

$\text{CH}_3\text{OH}\dots\text{HCl}$, $\text{CO}_2\dots\text{HCl}$ are also discussed for illustrating MESP features.

3.1 Geometry and Interaction Energy

The geometries of two representative cases from each category are presented in Figure 1 along with non-covalent interaction distance (d). The d value of all the systems are presented in Table 2 along with BSSE corrected interaction energy (E_{int}).

Conventional hydrogen bonded complexes involving neutral molecules (HB1–HB6) show E_{int} in the range 2.3–7.4 kcal/mol. Similar E_{int} range is observed for halogen bonded systems (XB1 – XB6) and dihydrogen bonded systems (DHB1–DHB6). Compared to the anionic HB complexes ($\text{HB1}^- - \text{HB6}^-$) showing E_{int} in the range 1.5–24.1 kcal/mol, the cationic HB complexes ($\text{HB1}^+ - \text{HB6}^+$) display stronger interaction energy (7.3–32.2 kcal/mol). All the three cationic pnictogen complexes, *viz.*, $\text{F}_4^+\text{P}\dots\text{NH}_3$, $\text{H}_2\text{F}_2^+\text{P}\dots\text{NCNH}_2$, and $\text{H}_3\text{F}^+\text{P}\dots\text{NCCH}_3$ show high E_{int} , *viz.*, 46.2, 33.5, 31.9 kcal/mol, respectively, while the neutral pnictogen complexes display E_{int} in the range similar to the neutral HB complexes. Similarly, the charged chalcogen complexes, both anionic and cationic show high E_{int} (18.8–27.9 kcal/mol) compared to the neutral ones (2.5–3.7 kcal/mol). Among the LiB complexes, Li^+ interacting with the π -systems of pyrrole and phenol show high E_{int} , *viz.*, 37.9 and 35.2 kcal/mol, respectively, and the neutral Li compounds interacting with the lone pair of NH_3 , CH_2 and H_2O show relatively smaller values, *viz.*, 22.2, 19.6 and 17.9 kcal/mol, respectively. In the case of tetrel complexes E_{int} are in the range 1.24–16.23 kcal/mol.

3.2 MESP V_{min} Analysis

According to the eDA description of non-covalent interactions, electron donation occurs from the electron

Table 1. Non-covalent complexes in various categories. Blue and red coloured atoms correspond to electron donor and electron acceptor atoms, respectively.

System	1	2	3	4	5	6
HB	$\text{HCHO}\dots\text{HF}$	$\text{Guanine}\dots\text{HCl}$	$\text{CH}_3\text{OH}\dots\text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{OH}\dots\text{HCl}$	$\text{Pyridine}\dots\text{C}_2\text{H}_2$	$\text{C}_4\text{H}_4\text{O}\dots\text{C}_4\text{H}_4\text{O}$
HB^+	$\text{HCN}\dots\text{H}_3\text{O}^+$	$\text{CH}_2\text{O}\dots\text{CH}_3\text{OH}_2^+$	$\text{NH}_3\dots\text{NH}_4^+$	$\text{CH}_3\text{OH}\dots\text{CH}_3\text{NH}_3^+$	$\text{H}_2\text{O}\dots\text{NH}_4^+$	$\text{CF}_3\text{CN}\dots\text{NH}_4^+$
HB^-	$\text{F}^-\dots\text{H}_2\text{O}$	$\text{NH}_2^-\dots\text{CF}_3\text{H}$	$\text{CH}_3\text{NH}^-\dots\text{CF}_3\text{H}$	$\text{Cl}^-\dots\text{HF}$	$\text{HO}^-\dots\text{HC}_5\text{H}_4\text{N}$	$\text{CH}_3\text{O}^-\dots\text{HCHO}$
CB	$\text{Cl}^-\dots\text{SeClF}$	$\text{H}_3\text{N}\dots(\text{OH})\text{H}_2\text{S}^+$	$\text{Cl}^-\dots\text{SFCl}$	$\text{NH}_3\dots\text{NH}_2\text{H}_2\text{S}^+$	$\text{HCN}\dots\text{SOFCl}$	$\text{C}_2\text{H}_2\dots\text{SF}_2$
PB	$\text{F}_4^+\text{P}\dots\text{NH}_3$	$\text{H}_2\text{F}_2^+\text{P}\dots\text{NCNH}_2$	$\text{H}_3\text{F}^+\text{P}\dots\text{NCCH}_3$	$\text{H}_2\text{FP}\dots\text{NH}_3$	$\text{H}_2\text{O}\dots\text{C}_5\text{NH}_4\text{PF}_2$	$\text{PCl}(\text{CN})_2\dots\text{PCl}(\text{CN})_2$
XB	$\text{H}_3\text{N}\dots\text{ClF}$	$\text{H}_3\text{N}\dots\text{BrCN}$	$\text{HCN}\dots\text{BrCF}_3$	$\text{ClCN}\dots\text{ClCF}_3$	$\text{H}_3\text{N}\dots\text{ClHSe}$	$\text{BrCN}\dots\text{BrCH}_3$
TB	$\text{LiCN}\dots\text{GeF}_4$	$\text{C}_6\text{H}_5\text{CN}\dots\text{GeF}_3\text{CN}$	$\text{MgHF}\dots\text{SiH}_3\text{CN}$	$\text{HCHO}\dots\text{CO}_2$	$\text{BeH}_2\dots\text{SiH}_3\text{F}$	$\text{NO}_2\text{C}_6\text{H}_4\text{CN}\dots\text{CF}_3\text{CN}$
LiB	$\text{Pyrrole}\dots\text{Li}^+$	$\text{Phenol}\dots\text{Li}^+$	$\text{H}_3\text{N}\dots\text{LiCN}$	$\text{H}_2\text{C}\dots\text{LiBr}$	$\text{H}_2\text{O}\dots\text{LiH}$	$\text{H}_2\text{O}\dots\text{LiF}$
DHB	$\text{NaH}\dots\text{HCN}$	$\text{MgH}_2\dots\text{HCN}$	$\text{MgH}_2\dots\text{HBr}$	$\text{AlH}_3\dots\text{HF}$	$\text{BeH}_2\dots\text{HC}_4\text{H}_4\text{N}$	$\text{AlH}_3\dots\text{HBr}$

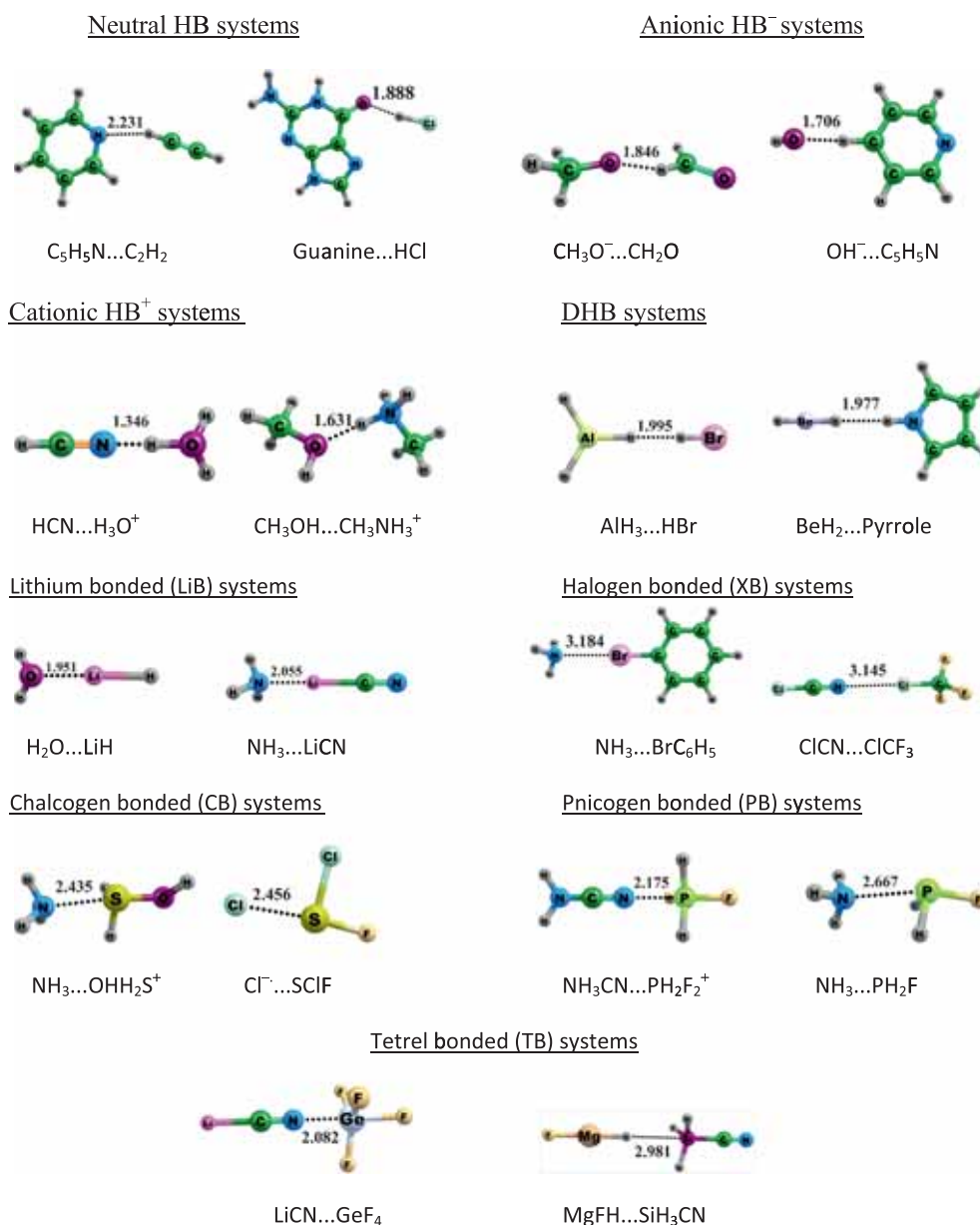


Figure 1. Optimized geometries of a representative set of non-covalent complexes. All bond lengths in Å.

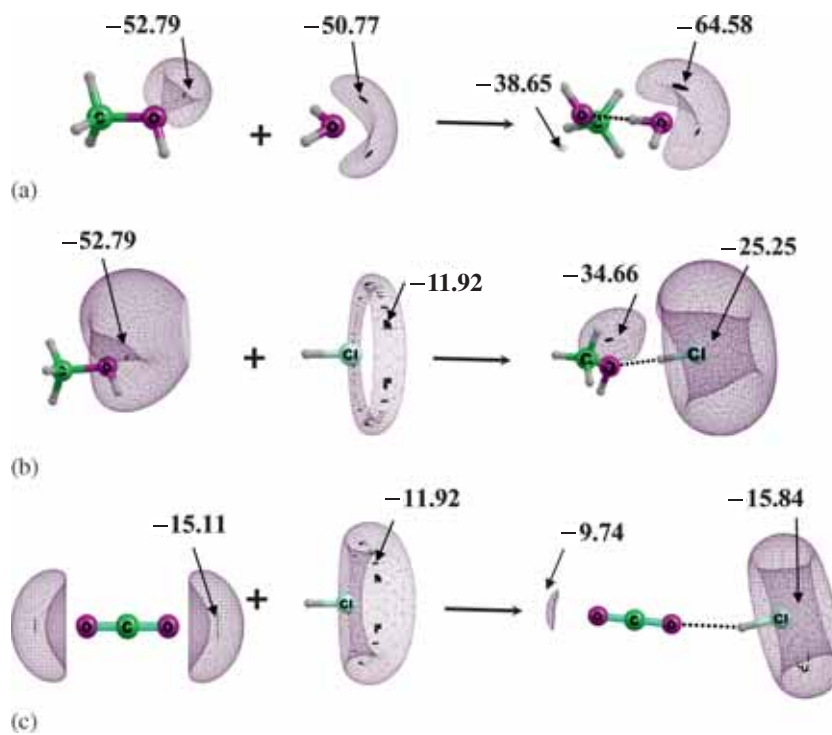
rich site of the donor molecule to the electron deficient site of the acceptor molecule. As a result, acceptor molecule of the eDA complex becomes electron rich at the expense of the donor molecule. The illustration of this feature can be readily obtained from V_{\min} analysis. From free molecules to eDA complex, a positive change in V_{\min} indicates the loss of electron density while a negative change in V_{\min} indicates the gain of electron density. For instance, by comparing the values of V_{\min} of the conventional HB complex, CH3OH...H2O (HB3) and its isolated monomers (Figure 2a), we can observe that V_{\min} of CH3OH becomes less negative (-38.65 kcal/mol) in the complex than the free molecule (-52.79 kcal/mol) while

that of H2O becomes more negative (-64.58 kcal/mol) than the free molecule (-50.77 kcal/mol). This indicates the electron flow from the donor molecule CH3OH to the acceptor molecule H2O. The V_{\min} of CH3OH...HCl (Figure 2b) shows that CH3OH as electron donor is more effective for HCl acceptor whereas V_{\min} of OCO...HCl indicates that the accepting power of HCl becomes weak when OCO is acting as electron donor (Figure 2c).

Similarly in dihydrogen bonded complexes, for example, MgH2...HCN (DHB5), V_{\min} of MgH2 at the electron donating site H becomes less negative in the complex compared to the isolated monomer whereas lone pair region of acceptor molecule HCN becomes

Table 2. d in Å and E_{int} in kcal/mol.

Complex	d (Å)	E_{int} (kcal/mol)	Complex	d (Å)	$E_{\text{int(B)}}$ (kcal/mol)
HB1	1.755	7.37	PB4	2.667	6.03
HB2	1.888	6.63	PB5	2.881	3.83
HB3	1.895	4.98	PB6	3.337	1.52
HB4	2.000	4.31	XB1	2.310	7.04
HB5	2.231	3.86	XB2	2.932	5.57
HB6	2.613	2.30	XB3	3.168	2.57
HB1 ⁺	1.346	32.20	XB4	3.145	1.88
HB2 ⁺	1.371	25.99	XB5	3.080	1.28
HB3 ⁺	1.577	24.98	XB6	3.345	0.70
HB4 ⁺	1.631	19.30	TB1	2.082	16.03
HB5 ⁺	1.649	19.29	TB2	2.251	5.13
HB6 ⁺	1.812	15.38	TB3	2.981	2.14
HB1 ⁻	1.387	24.11	TB4	2.877	1.94
HB2 ⁻	1.761	22.23	TB5	2.924	1.69
HB3 ⁻	1.731	22.21	TB6	3.440	1.24
HB4 ⁻	1.893	21.50	LiB1	1.927	37.90
HB5 ⁻	1.706	17.99	LiB2	1.889	35.21
HB6 ⁻	1.846	15.54	LiB3	2.055	22.20
CB1	2.467	27.92	LiB4	2.188	19.58
CB2	2.435	24.51	LiB5	1.951	15.86
CB3	2.456	22.44	LiB6	1.961	15.63
CB4	2.672	18.78	DHB1	1.803	9.00
CB5	3.008	3.66	DHB2	1.995	3.74
CB6	3.140	2.50	DHB3	1.747	3.67
PB1	1.923	46.21	DHB4	1.683	3.21
PB2	2.175	33.46	DHB5	1.977	2.14
PB3	2.281	31.88	DHB6	1.995	1.71

**Figure 2.** MESP isosurface plots for hydrogen bonded (HB) complexes and monomers at values (a) -37.65 , (b) -11.30 (c) -9.41 kcal/mol. V_{min} values are also indicated in kcal/mol.

more negative than the isolated molecule (Figure 3a). The V_{\min} illustrations given in Figure 3b and 3c, for $\text{MgH}_2 \dots \text{HBr}$ and $\text{AlH}_3 \dots \text{HBr}$, respectively, suggest that the donating power of the donor molecule is strongly related with the accepting power of the acceptor molecule and vice versa.

Similar observations hold good for all the other type of complexes wherein V_{\min} can be determined for the donor and acceptor sites (cationic systems are devoid of V_{\min}). The V_{\min} illustrations using the halogen bonded $\text{BrCN} \dots \text{CH}_3\text{Br}$ (XB6) is presented in Figure 4.

The change in V_{\min} of donor molecule ($\Delta V_{\min}(\text{D})$) and that of acceptor molecule ($\Delta V_{\min}(\text{A})$) can be considered as the electron donating and accepting power of the donor and acceptor, respectively. Further, according to Mohan and Suresh, the difference between $\Delta V_{\min}(\text{D})$

and $\Delta V_{\min}(\text{A})$, referred to as $\Delta\Delta V_{\min}$ has to be proportional to E_{int} (Table 3).⁶¹ The linear correlation between $\Delta\Delta V_{\min}$ and E_{int} given in Figure 5 confirms this hypothesis for all the available systems. Since certain molecules or complexes are devoid of V_{\min} , its use to interpret the interaction energy for all types of non-covalent complexes is not possible.

3.3 MESP V_n Analysis

The MESP value at the donor atom $V_n(\text{D})$ and the acceptor atom $V_n(\text{A})$ undergoes significant change during the non-covalent eDA complex formation. The change in MESP observed for the donor atom ($\Delta V_n(\text{D})$) is proportional to the electron donating ability of the donor molecule while that observed for the acceptor

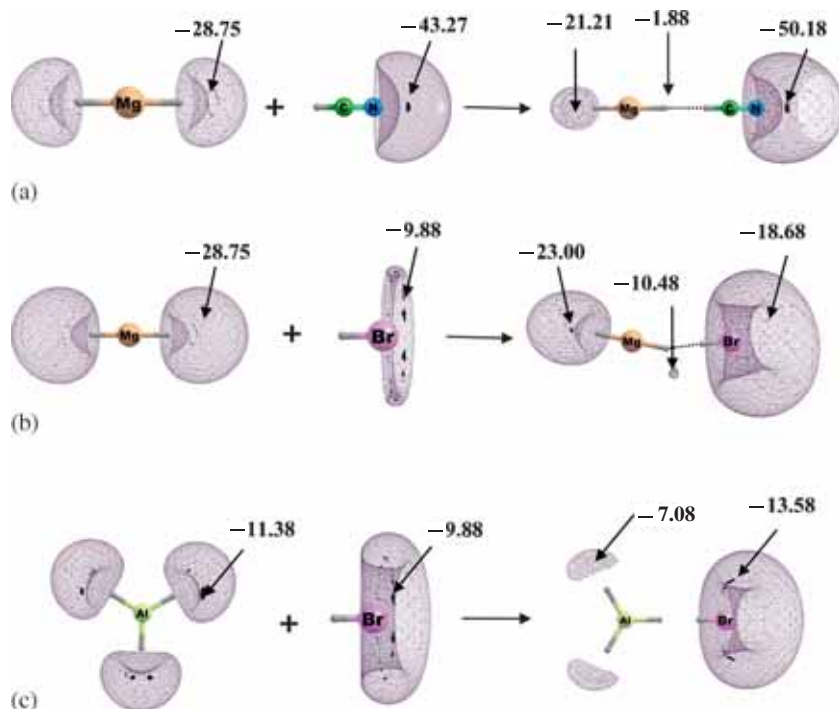


Figure 3. MESP isosurface plots for dihydrogen bonded (HB) complexes and monomers at values (a) -18.83 , (b) -9.41 (c) -6.28 kcal/mol. V_{\min} values are also indicated in kcal/mol.

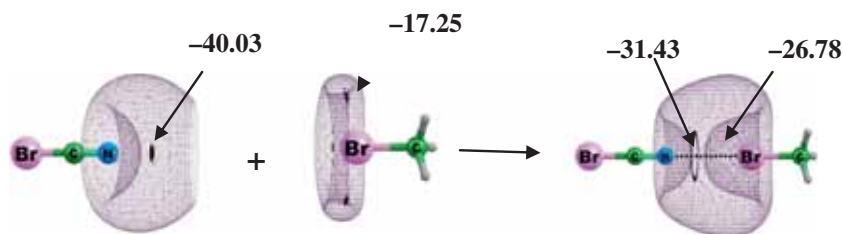


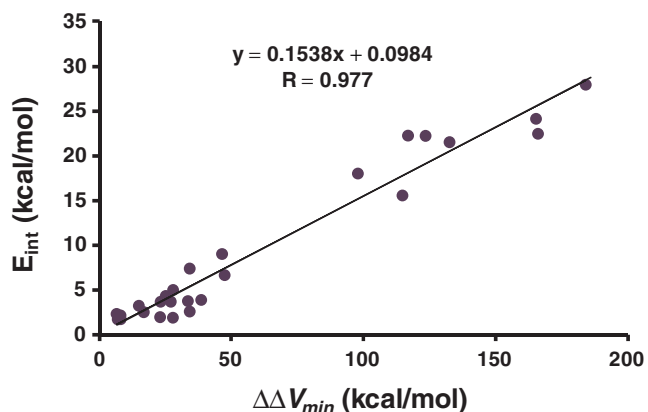
Figure 4. MESP isosurface plots for halogen bonded (HB) complex and monomers at value -14.43 kcal/mol. V_{\min} values are also indicated in kcal/mol.

Table 3. MESP parameters in kcal/mol for all the non-covalent complexes.

Complex	$\Delta V_{\min}(\text{D})$	$\Delta V_{\min}(\text{A})$	$\Delta\Delta V_{\min}$
HB1	16.18	-18.03	34.21
HB2	21.21	-26.24	47.45
HB3	14.14	-13.81	27.95
HB4	14.34	-10.83	25.17
HB5	29.03	-9.24	38.57
HB6	2.94	-3.63	6.58
HB1 ⁻	34.92	-130.26	165.17
HB2 ⁻	25.65	-91.12	116.77
HB3 ⁻	26.32	-97.07	123.39
HB4 ⁻	18.99	-113.47	132.46
HB5 ⁻	26.71	-71.1	97.81
HB6 ⁻	21.71	-92.93	114.65
CB1	63.77	-120.17	183.94
CB3	51.19	-114.72	165.9
CB5	10.37	-12.85	23.21
CB6	9.88	-6.96	16.84
XB3	27.46	-6.75	34.22
XB4	21.88	-5.98	27.86
TB4	11.11	-11.94	23.04
TB5	3.68	-3.35	7.03
DHB1	24.45	-22.02	46.47
DHB2	26.63	-6.91	33.54
DHB3	18.28	-8.80	27.08
DHB4	7.11	-7.89	15.01
DHB5	5.46	-2.60	8.06
DHB6	4.41	-3.70	8.11

Table 4. MESP parameters in kcal/mol for all the non-covalent complexes.

Complex	$\Delta V_n(\text{D})$	$\Delta V_n(\text{A})$	$\Delta\Delta V_n$
HB1	22.41	-24.92	47.33
HB2	12.09	-33.03	45.12
HB3	14.90	-19.78	34.44
HB4	15.4	-13.25	28.65
HB5	6.29	-15.02	21.31
HB6	4.22	-7.20	11.41
HB1 ⁺	138.31	-46.62	184.94
HB2 ⁺	134.04	-33.59	167.63
HB3 ⁺	131.89	-34.75	166.64
HB4 ⁺	114.32	-27.00	141.32
HB5 ⁺	125.26	-28.50	153.77
HB6 ⁺	92.88	-26.33	119.21
HB1 ⁻	42.28	-146.82	188.48
HB2 ⁻	19.90	-125.00	145.53
HB3 ⁻	21.34	-122.63	143.97
HB4 ⁻	22.38	-137.94	160.32
HB5 ⁻	26.67	-110.77	137.44
HB6 ⁻	20.26	-117.88	138.15
CB1	63.77	-120.17	183.94
CB2	134.33	-27.25	161.58
CB3	51.19	-114.72	165.90
CB4	112.54	-22.35	134.88
CB5	10.37	-12.85	23.21
CB6	9.88	-6.96	16.84
PB1	218.53	-49.67	268.2
PB2	130.56	-46.67	177.23
PB3	124.28	-41.06	165.34
PB4	20.56	-18.70	39.26
PB5	13.68	-9.16	22.84
PB6	5.43	5.42	0.01
XB1	38.58	-23.06	61.63
XB2	20.19	-16.08	36.26
XB3	7.30	-11.65	18.94
XB4	4.64	-10.52	15.16
XB5	0.39	-9.51	9.90
XB6	-2.06	-10.52	8.45
TB1	57.55	-56.28	113.83
TB2	38.36	-30.51	68.86
TB3	8.48	-4.67	13.15
TB4	5.25	-14.67	19.93
TB5	7.88	-5.31	13.29
TB6	2.45	-8.94	11.39
LiB1	130.08	-89.70	219.78
LiB2	119.30	-92.21	211.51
LiB3	61.10	-54.98	116.08
LiB4	52.16	-52.37	104.52
LiB5	54.31	-47.60	101.91
LiB6	54.96	-49.44	104.41
DHB1	2.87	-37.79	40.66
DHB2	11.87	-13.52	25.4
DHB3	9.71	-9.05	18.76
DHB4	13.64	-11.62	25.26
DHB5	12.68	-5.95	18.62
DHB6	8.39	-4.30	12.69

**Figure 5.** Plot showing the linear correlation between $\Delta\Delta V_{\min}$ and E_{int} for the non-covalent complexes.

atom ($\Delta V_n(\text{A})$) is proportional to the electron accepting power of the acceptor molecule. On the basis of this interpretation, Mohan and Suresh have shown that the difference between $\Delta V_n(\text{D})$ and $\Delta V_n(\text{A})$, referred to as $\Delta\Delta V_n$ (Table 4) is proportional to the E_{int} of the complex.⁶¹ This hypothesis is valid for all the complexes studied herein as a good linear correlation between $\Delta\Delta V_n$ and E_{int} exists (Figure 6).

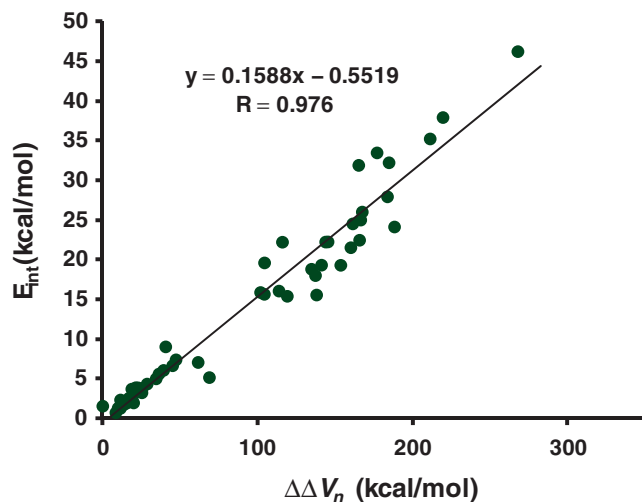


Figure 6. Plot showing the linear correlation between $\Delta\Delta V_n$ and E_{int} for all the non-covalent complexes.

Table 5. MESP parameters and interaction energy (E_{int}) in kcal/mol (solvent phase) for a representative set of non-covalent complexes.

Complex	$\Delta V_n(D)$	$\Delta V_n(A)$	$\Delta\Delta V_n$	E_{int}
HB1	28.51	-42.95	71.46	7.54
HB3	17.85	-27.33	45.18	4.99
HB1 ⁺	140.48	-54.64	195.12	14.05
HB2 ⁺	141.79	-42.52	184.31	13.99
HB1 ⁻	32.48	-165.30	197.78	9.48
HB2 ⁻	22.53	-154.52	177.05	6.38
CB5	15.79	-18.06	33.85	4.76
CB6	13.36	-8.11	21.47	4.03
PB4	49.19	-26.16	75.34	10.06
PB5	18.26	-12.47	30.73	4.63
XB1	134.04	-31.19	165.23	23.28
XB2	28.42	-17.97	46.39	7.13
TB1	78.15	-74.93	153.08	28.16
TB3	26.66	-8.87	35.53	3.12
LiB3	70.29	-53.60	123.89	20.17
LiB5	62.16	-53.77	115.92	13.85
DHB2	28.50	-23.49	51.99	2.11
DHB4	24.38	-16.15	40.53	2.59

MP4/Aug-cc-pvDZ-SMD/MP2/6-311++g(d,p)-SMD level interaction energy (E_{int}) and MESP properties of two complexes from each category are summarised in Table 5. The $\Delta\Delta V_n$ correlates linearly with E_{int} in the case of neutral complexes whereas charged species deviates significantly from this plot. This can be attributed to the large solvation effect experienced by the charged species as their solvation effect incorporated interaction energy is much lower than the gas phase results (Figure 7).

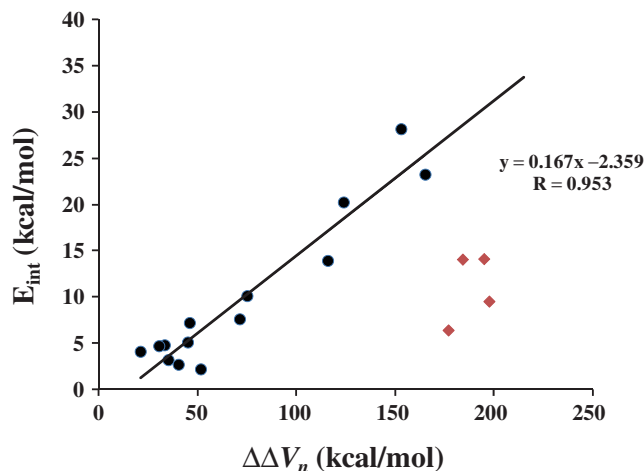


Figure 7. Plot showing the linear correlation between $\Delta\Delta V_n$ and E_{int} for a representative set of neutral complexes in solvent phase. Circle and diamond symbols represent neutral and charged complexes, respectively.

4. Conclusions

High accuracy *ab initio* calculations have been performed on a large variety of non-covalent dimers in order to investigate the applicability of molecular electrostatic potential (MESP) based parameters to interpret the non-covalent bond formation. This type of analysis has been previously reported for the well established interactions such as hydrogen, dihydrogen and halogen bonds and interpreted them as electron donor-acceptor (eDA) interactions.⁶¹ The results presented in this study clearly suggest that the non-covalent interactions present in lithium bond, tetrel bond, pnictogen bond and chalcogen bond can be grouped under the general category of eDA interactions. The eDA complex formation for a representative set of complexes has been illustrated using MESP isosurface and MESP minimum (V_{min}). The electron donating ability of the donor molecule is obtained in terms of the difference between change in V_{min} of the donor molecule or the change in V_n of the donor atom with respect to the eDA complex while the electron accepting ability of the acceptor is related with the corresponding V_{min} or V_n change at the acceptor molecule or the acceptor atom. The interaction energy is found to be the highest when a strongly electron donating molecule interacts with a strongly electron accepting molecule. The good linear correlations obtained between $\Delta\Delta V_{min}$ and E_{int} as well as between $\Delta\Delta V_n$ and E_{int} validate the interpretation that in any-type of non-covalent complexes studied herein, certain degree of electron donation and acceptance occurs which is directly proportional to the energy released during bond formation. Thus, in agreement with Mohan and Suresh,⁶¹ the MESP based eDA concept holds good

for all type of non-covalent interactions that have been analyzed in the gas phase. Calculations on a representative set of molecules have shown that in solvent phase, $\Delta\Delta V_n$ versus E_{int} linear correlation is valid for neutral complexes whereas the charged species may deviate from this plot due to large changes in the interaction energy.

Supplementary Information (SI)

SCF energies and BSSE for MP2 and MP4 methods are given in the Supplementary Information, available at www.ias.ac.in/chemsci.

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