# A Molecular Electrostatic Potential Analysis of Hydrogen, Halogen, and Dihydrogen Bonds

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S *Supporting Information*

ABSTRACT: Hydrogen, halogen, and dihydrogen bonds in weak, medium and strong regimes (<1 to ~60 kcal/mol) have been investigated for several intermolecular donor−acceptor (D-A) complexes at ab initio MP4//MP2 method coupled with atoms-in-molecules and molecular electrostatic potential (MESP) approaches. Electron density ρ at bond critical point correlates well with interaction energy (E_{nb}) for each homogeneous sample of complexes, but its applicability to the entire set of complexes is not satisfactory. Analysis of MESP minimum (V_{min}) and MESP at the nuclei (V_n) shows that in all D-A complexes, MESP of A becomes more negative and that of D becomes less negative suggesting donation of electrons from D to A leading to electron donor−acceptor (eDA) interaction between A and D. MESP based parameter $\Delta\Delta V_n$ measures donor−acceptor strength of the eDA interactions as it shows a good linear correlation with E_{nb} for all D-A complexes ($R^2 = 0.976$) except the strongly bound bridged structures. The bridged structures are classified as donor−acceptor−donor complexes. MESP provides a clear evidence for hydrogen, halogen, and dihydrogen bond formation and defines them as eDA interactions in which hydrogen acts as electron acceptor in hydrogen and dihydrogen bonds while halogen acts as electron acceptor in halogen bonds.
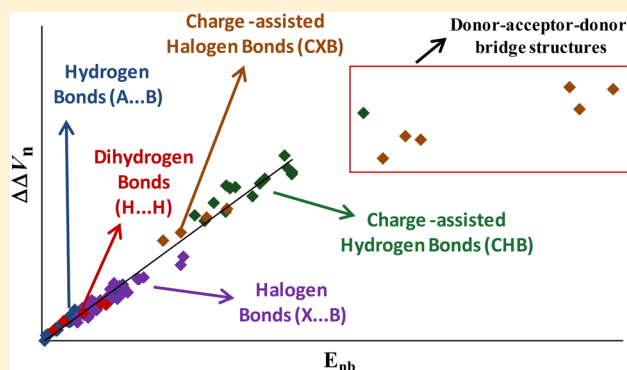
INTRODUCTION

Hydrogen bonding is one of the most important, widely discussed and highly debated interactions in chemistry. Enormous theoretical and experimental efforts[1−12] has been made to understand hydrogen bonds due to their crucial roles in controlling and stabilizing molecular self-assembly and in mediating dynamic processes. Desiraju[2] described it as an "interaction without borders" to express the large variations in covalent, electrostatic, and van der Waals energy components of a hydrogen bond. Despite the extensive research over years, the perception of hydrogen bonds continues to evolve and a universally accepted definition of hydrogen bond remains elusive in the literature. A task group of IUPAC has reviewed this topic in depth based on theoretical and experimental knowledge acquired over the past century and proposed a short modern definition for it.[13,14] According to IUPAC definition, hydrogen bond is "an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X−H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation". This definition covers weak (<4 kcal/mol), moderate (4−15 kcal/mol), and strong (15−40 kcal/mol)[15] hydrogen bonds. Halogen bonds are highly directional noncovalent interactions that occur between an electron donor and a halogen atom in another molecule.

Recently, IUPAC recommendations[16] 2013 proposed a definition for halogen bonds according to which "halogen bonds occur when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity". Politzer et al.[17−21] demonstrated that halogen bond is an electrostatically driven interaction between positive σ-hole (a region of positive electrostatic potential on the outer side of the halogen) of the halogen and the negative potential of the base. Although hydrogen bonds and halogen bonds fall in different categories, numerous properties of them run in parallel in terms of strength and directionality.[22−26] Crabtree and co-workers[27] showed that hydrogen atom in metal hydrides and H_3NBH_3 can form unusual hydrogen bonding interaction with a hydrogen atom in another molecule. The resulting H...H interactions are called dihydrogen bonds. In systems showing hydrogen bonds, halogen bonds, and dihydrogen bonds, one atom in the bonded region accepts electron density from the other[28−30] and hence these interactions can be viewed as

interaction between a Lewis base acting as electron donor (D) and a Lewis acid acting as electron acceptor (A).

Bader's "atoms in molecules" (AIM)[31−33] and molecular electrostatic potential (MESP)[19,34−37] analyses are important theoretical tools for eliciting noncovalent interactions. Numerous studies[38−43] have shown that AIM topological parameters viz. electron density (ρ) at the bond critical point (bcp) and its Laplacian ($\nabla^2\rho$) are important quantities to characterize the strength and nature of hydrogen bonds, halogen bonds, and dihydrogen bonds. There have been various reports[7,38−42] where ρ correlates with the interaction energy and length of the hydrogen bond. Sathyamurthy[40] et al. attempted to understand the concept of hydrogen bonding without borders using the topological properties of electron density and showed that the electron density at the hydrogen bond critical point increases approximately linearly with increasing stabilization energy in going from weak to moderate and strong hydrogen bonds. The most negative valued MESP point of a molecule, designated as V_{min}, symbolizes the sites of electron localization in a molecule[44,45] and has been used successfully in predicting the sites and directionality of hydrogen bonds in a variety of systems.[10,46−51] Kollman et al.[10] showed the existence of good correlation between hydrogen bond energies and the magnitude of MESP at fixed distance from the proton acceptors in a series of complexes between HF and various acceptors. Recently, in a series of works[47,50,52−54] Galabov et al. showed that MESP at the site of electron donor atom could be successfully used as reactivity descriptor for the study of hydrogen bonding. However, most of these works consider hydrogen bond complexes with either donor or acceptor molecules fixed and hence the applicability of these parameters for a heterogeneous sample of complexes with different proton donors and/or acceptors is limited.

Herein, we show that for a large variety of intermolecular hydrogen bonds, halogen bonds, and dihydrogen bonds, a simple definition suggesting them as electron donor−acceptor (eDA) interaction holds good. Our results are based on high level ab initio interaction energy data and topographical features of ρ distribution and MESP. The value of ρ at bcp, V_{min} and V_n, are used as electronic descriptors to quantify the strength and characteristics of eDA interactions of a large variety of complexes. We show that among ρ, V_{min}, and V_n the last quantity is highly suited to measure the electron donating power of donor as well as electron accepting power of acceptor. A strong correlation between interaction energy and donor−acceptor strength is obtained for all the complexes which prove that they all belong to the same class, eDA complex.

■ COMPUTATIONAL METHODS

Geometry optimization of all noncovalent complexes are done at ab initio second-order Møller−Plesset perturbation theory[55] method, MP2 using 6-311++G(d,p) basis set. Vibrational frequency analyses are performed to ensure that all the structures correspond to true energy minima containing only real frequencies. MP4 single point energy calculation aug-cc-pvtz is performed on the MP2 optimized geometries to obtain more accurate energies. The nonovalent interaction energies (E_{nb}) are calculated using supermolecule approach (i.e., interaction energy of the complex = energy of the complex − energy of the reactants optimized separately) with the correction for the basis set superposition error (BSSE) by using the Boys and Bernardi[56] counterpoise technique. Gaussian09[57] suite of programs is employed for all the

computations. The topological properties of electron density at bond critical points (bcp) have been studied using AIM methodology with AIM2000 program.[58,59] MESP topographical analysis of the monomers and the intermolecular complexes are carried out at MP4/aug-cc-pvtz level. MESP at any point with the position vector **r** can be calculated using the equation,

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

where Z_A is the nuclear charge of atom A with radius vector $\mathbf{R}_A$. $\rho(\mathbf{r}')$ is the electron density of the molecule and $\mathbf{r}'$ is a dummy integration variable.[60,61] $V(\mathbf{r})$ is strongly dependent on the local charges around point **r**, the positive charges on the neighboring nuclei, and the electron density in closer vicinity of point **r**. V_{min} have been located for the donor and acceptor molecules in their isolated and bound state in the noncovalent complex. MESP at the nuclei of the atoms participating in the nonbonded interactions is also evaluated. MESP at the nucleus "A" of a molecule (V_n) can be obtained by dropping out the nuclear contribution due to Z_A from the definition of MESP, via eq 2.

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

The nuclei centered quantity, V_n measures the electrostatic potential at the position of the atom "n" due to all the electrons and rest of the nuclei. It is a local molecular property associated with the particular atom center. MESP at each atom of the donor and acceptor molecules is obtained from the standard output of the Gaussian09 program.

■ RESULTS AND DISCUSSION

A total of 104 intermolecular noncovalent complexes are selected for this study that are classified into four categories, viz. (i) hydrogen bonds in neutral complexes (A...B), (ii) charge-assisted hydrogen bonds (CHB), (iii) halogen bonds (X...B), (iv) charge-assisted halogen bonds (CXB), and (v) dihydrogen bonds (H...H). The category A...B includes complexes where both donor and acceptor molecules are neutral; it has three subclasses: C−H...Y (hydrogen bonds formed between C−H of C_2H_2, CF_3H, and CH_4 and conventional electron donor molecules), X−H...π (hydrogen bonds where the electron donor is a π-system), and X−H...Y (hydrogen bonds with HCl, HF, H_2O, PH_3, H_2S, CH_3OH, and HBr as electron donors/ acceptors) complexes. In halogen bonds, an electrostatic interaction exists between the positive potential of halogen and the lone pair center. We have considered the complexes of diatomic interhalogen compounds IF, ICl, IBr, ClF, BrF, and BrCl with Lewis bases H_2S, NH_3, H_2O, HCN, $NCCH_3$, and OCH_2. CHB and CXB includes noncovalent complexes connected through relatively strong hydrogen bonds and halogen bonds, respectively, where either the donor or acceptor species is charged, that is, hydrogen/halogen bonds in anionic systems and cationic systems. These bonds are characterized by their partial covalent character.[2,5,62,63] We have also included dihydrogen bond complexes of BeH_2, LiH, NaH, and BH_4^- (electron donors) with different electron acceptors. Throughout this paper, E_{nb} represents the interaction energy calculated at MP4//MP2 method and the standard notations ρ and $\nabla^2\rho$ are used to indicate the electron density at the bond critical point (bcp) of the electron donor−acceptor bond and the Laplacian of the electron density at the bcp.
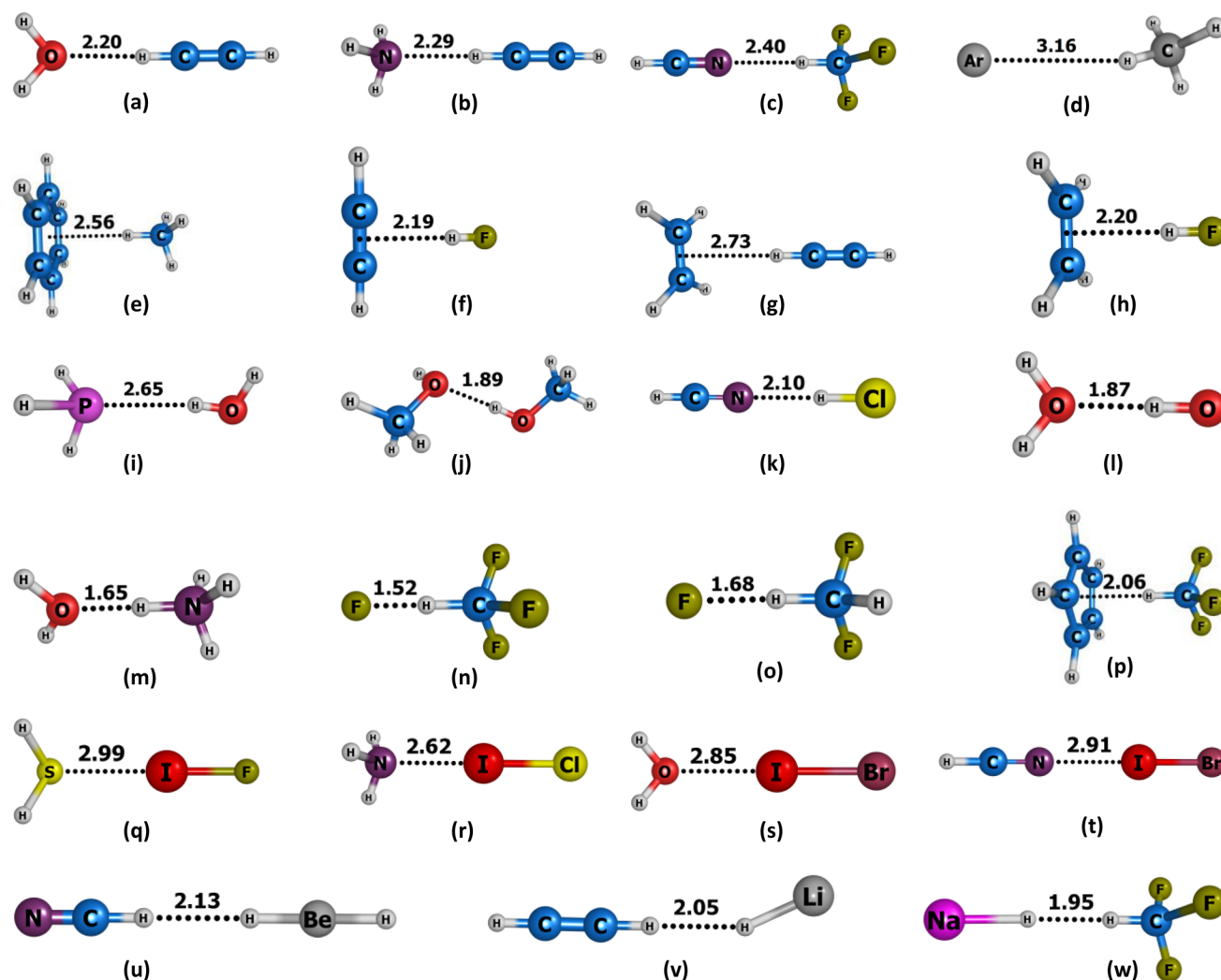
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Figure 1. Representative set of intermolecular hydrogen and halogen bonded complexes studied: (a) $H_2O\cdots HCCH$, (b) $H_3N\cdots HCCH$, (c) $HCN\cdots HCF_3$, (d) $Ar\cdots HCH_3$, (e) $H_6C_6\cdots HCH_3$, (f) $H_2C_2\cdots HF$, (g) $H_4C_2\cdots HCCH$, (h) $H_4C_2\cdots HF$, (i) $H_3P\cdots H_2O$, (j) $H_3CHO\cdots HOCH_3$, (k) $HCN\cdots HCl$, (l) $H_2O\cdots H_2O$, (m) $H_2O\cdots H_4^+N$, (n) $F^-\cdots HCF_3$, (o) $F^-\cdots H_2CF_2$, (p) $H_5C_5\cdots HCF_3$, (q) $H_2S\cdots IF$, (r) $H_3N\cdots ICl$, (s $H_2O\cdots IBr$, (t) $HCN\cdots IBr$, (u) $HBeH\cdots HCN$, (v) $LiH\cdots HCCH$, (w) $NaH\cdots HCF_3$. Bond distances in Å.

Optimized geometries of a representative set of complexes are given in Figure 1. The accuracy of E_{nb} calculated with MP4//MP2 method is very close to the "gold standard" CCSD(T) benchmark values available in the literature with mean absolute deviation 0.25 kcal/mol (Supporting Information). The E_{nb} values range from <1 to 59 kcal/mol and covers very weak, medium, and strong interactions.

Table 1 presents the E_{nb} values of a representative set of complexes along with ρ and $\nabla^2\rho$ at bcp. The values of ρ and $\nabla^2\rho$ for H⋯H and most of the A⋯B complexes fall in the typical range[43] proposed for ρ (0.002−0.035 au) and $\nabla^2\rho$ (0.024−0.139 au) in hydrogen bond complexes. However, for most of XB, CHB, and CXB complexes, higher values of ρ and $\nabla^2\rho$ are observed indicating the presence of remarkably stronger interactions. Nonetheless, except $H_3O^+\cdots H_2O$, all other D-A systems exhibit typical closed-shell interactions by virtue of their positive $\nabla^2\rho$ values. $H_3O^+\cdots H_2O$ corresponds to a Zundel ion[64] and have a $\nabla^2\rho$ value of −0.564 au, which is characteristic of a bond with covalent nature. Anionic CXB complexes viz. $F^-\cdots IF$, $F^-\cdots BrF$, $Cl^-\cdots IF$, $Cl^-\cdots BrF$, $F^-\cdots IBr$, and $Cl^-\cdots IBr$ are characterized by bridged structures and exceptionally high interaction energy values which fall in the range of −35 to −59

kcal/mol (Figure 2). For instance, in the case of $F^-\cdots IF$ the position of I is symmetric with respect to both the F atoms meaning that the complex is a resonance combination of $F^-\cdots IF$ and $F\cdots IF^-$. Similar bonding scenario is seen in $F^-\cdots BrF$, $Cl^-\cdots IF$, $Cl^-\cdots BrF$, $F^-\cdots IBr$, and $Cl^-\cdots IBr$. The cationic complex $H_3O^+\cdots H_2O$ also exhibits a bridged configuration ($H_2O\cdots H^+\cdots OH_2$) with the H^+ placed at 1.19 and 1.20 Å from each of the two H_2O molecules (Figure 2).
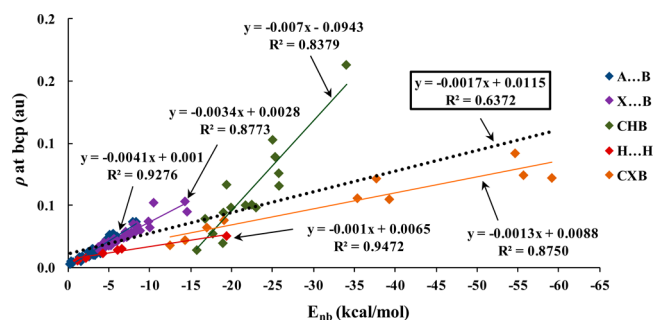
It is well established that the topological parameters at bcp correlate with E_{nb} for a variety of noncovalent complexes. Sathyamurthi et al.[40] showed a linear relationship between ρ and E_{nb} as well as $\nabla^2\rho$ and E_{nb} for a set of intermolecular complexes of varying strengths ranging from van der Waals to covalent limit. They also demonstrated a smooth change in the nature of the noncovalent interaction from van der Waals to classical hydrogen bonding and strong hydrogen bonding. Analysis of the data presented in Table 1 suggest that the correlation between ρ and E_{nb} (Figure 3) is very good for each homogeneous sample of complexes. However, the correlation is found to be poor ($R^2 = 0.64$) for the heterogeneous sample of complexes comprising of neutral (A⋯B), halogen-bonded (X⋯B), dihydrogen-bonded (H⋯H), charge-assisted hydro-

Table 1. Interaction Energies (E_{nb}), AIM Properties (ρ and $\nabla^2\rho$) and MESP Features (ΔV_{min-A}, ΔV_{min-D}, $\Delta\Delta V_{min}$, ΔV_{n-A}, ΔV_{n-D}, and $\Delta\Delta V_n$) for Representative Set of Intermolecular Complexes

complex	E_{nb} (kcal/mol)	ρ (au)	$\nabla^2\rho$ (au)	ΔV_{min-A} (kcal/mol)	ΔV_{min-D} (kcal/mol)	$\Delta\Delta V_{min}$ (kcal/mol)	ΔV_{n-A} (au)	ΔV_{n-D} (au)	$\Delta\Delta V_n$ (au)
Ar...HCH$_3$	−0.23	0.003	0.011				−0.0005	0.0005	0.0009
H$_2$S...HCH$_3$	−0.37	0.005	0.016	−4.15	0.56	4.72	−0.0088	0.0007	0.0096
H$_3$P...H$_2$S	−1.47	0.008	0.020				−0.0097	0.0080	0.0177
H$_2$S...H$_2$S	−1.38	0.008	0.024	−4.14	4.39	8.53	−0.0087	0.0091	0.0178
H3P...H$_2$O	−2.47	0.013	0.031				−0.0185	0.0134	0.0319
H$_4$C$_2$...HF	−4.47	0.018	0.040	−10.10	14.33	24.43	−0.0253	0.0257	0.0510
H$_3$P...H$_3$P	−0.62	0.004	0.011	−3.66	9.89	13.55	−0.0075	0.0023	0.0098
H$_2$O...H$_2$O	−4.70	0.023	0.085	−13.37	15.94	29.30	−0.0303	0.0260	0.0563
H$_3$BH$^-$...HF	−19.38	0.025	0.057	−105.30	15.88	121.17	−0.2005	0.0423	0.2428
HBeH...HCCH	−1.17	0.006	0.018	−2.81	2.49	5.30	−0.0079	0.0098	0.0176
LiH...HCCH	−4.26	0.011	0.027	−18.37	10.29	28.66	−0.0413	0.0041	0.0454
LiH...HCF$_3$	−6.06	0.014	0.033	−15.89	20.71	36.60	−0.0473	0.0121	0.0594
CF$_3$H...HNa	−6.57	0.015	0.033	−18.34	18.89	37.22	−0.0537	0.0195	0.0732
H$_2$O...H$_4$N$^+$	−19.93	0.048	0.127				−0.0434	0.2011	0.2445
C$_6$H$_6$...H$_4$N$^+$	−18.93	0.020	0.054				−0.0519	0.1537	0.2055
ClO$^-$...H$_2$O	−19.38	0.067	0.125	−113.14	20.33	133.47	−0.2028	0.0405	0.2433
ClO$^-$...HF	−22.46	0.051	0.155	−110.27	24.91	135.18	−0.2148	0.0355	0.2504
ClO$_2^-$...HF	−25.32	0.089	0.092	−117.53	17.70	135.22	−0.2190	0.0559	0.2750
H$_3$N...ClF	−10.46	0.052	0.139				−0.0398	0.0615	0.1013
H$_2$O...ClF	−4.95	0.021	0.101	−12.80	16.25	29.05	−0.0242	0.0315	0.0557
H$_2$S...ClF	−4.44	0.020	0.062	−10.92	10.98	21.90	−0.0172	0.0249	0.0420
HCN...BrCl	−4.30	0.015	0.065	−10.08	32.47	42.55	−0.0210	0.0208	0.0418
H$_3$CCN...BrCl	−5.24	0.018	0.075	−13.23	35.02	48.25	−0.0273	0.0202	0.0474
H$_2$CO...BrCl	−4.73	0.018	0.078	−8.73	10.48	19.21	−0.0159	0.0218	0.0377
F$^-$...FI	−59.15	0.072	0.283	−130.75	87.79	218.54	−0.2183	0.1817	0.4000
CH$_2$Cl$^-$...NH$_3$	−16.96	0.032	0.104				−0.0319	0.1645	0.1964
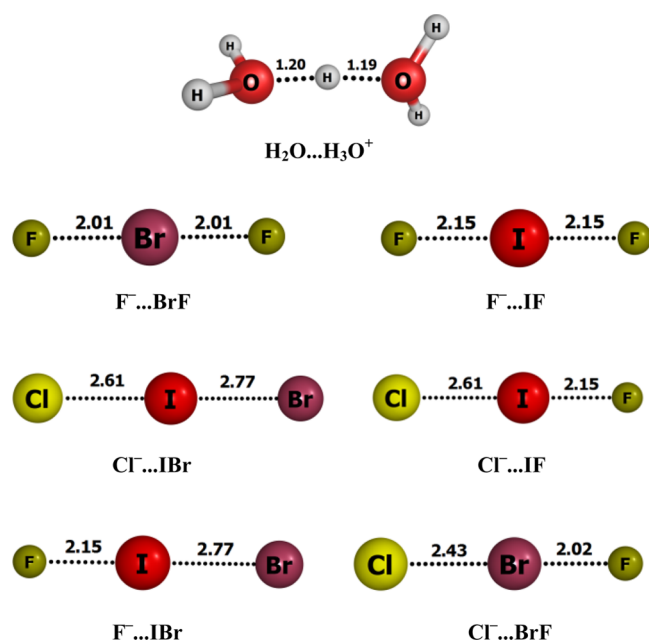
Figure 2. D-A complexes showing bridged configurations. Bond distances in Å.

Figure 3. Relationship between interaction energy (kcal/mol) and electron density (ρ) at bcp. The dotted line represents the overall correlation and the colored lines indicate the correlation for separate classes of noncovalent complexes.

gen-bonded (CHB), and charge-assisted halogen-bonded (CXB) systems. For instance, in A...B complexes E_{nb} versus ρ correlation holds good with R^2 value of 0.927. Likewise, satisfactory correlations exist for X...B, CHB, CXB and H...H bonds too with the R^2 values 0.877, 0.837, 0.875, and 0.947, respectively. Thus, although ρ at bcp correlates reasonably well with E_{nb} for each homogeneous sample of intermolecular complexes, its applicability for the whole set is not satisfactory. These results clearly suggest that the applicability of AIM parameters is not quite adequate to describe a large variety of complexes on a uniform scale.[7]

The recent IUPAC recommendations emphasize on the keywords "attractive interaction" and "evidence of bond formation" to define a hydrogen bond or halogen bond. Because bonding unequivocally means an attractive interaction, proving the bond formation with proper "evidence" attains paramount importance. An attractive or repulsive interaction is bound to change the ρ distribution and hence a very sensitive quantity directly related to ρ and amenable to experimental determination is highly useful to discover noncovalent bond formation. MESP is such a quantity and it connects ρ via eq 1. Any change in ρ distribution due to bond formation between D and A molecules will be well reflected in their MESP features.
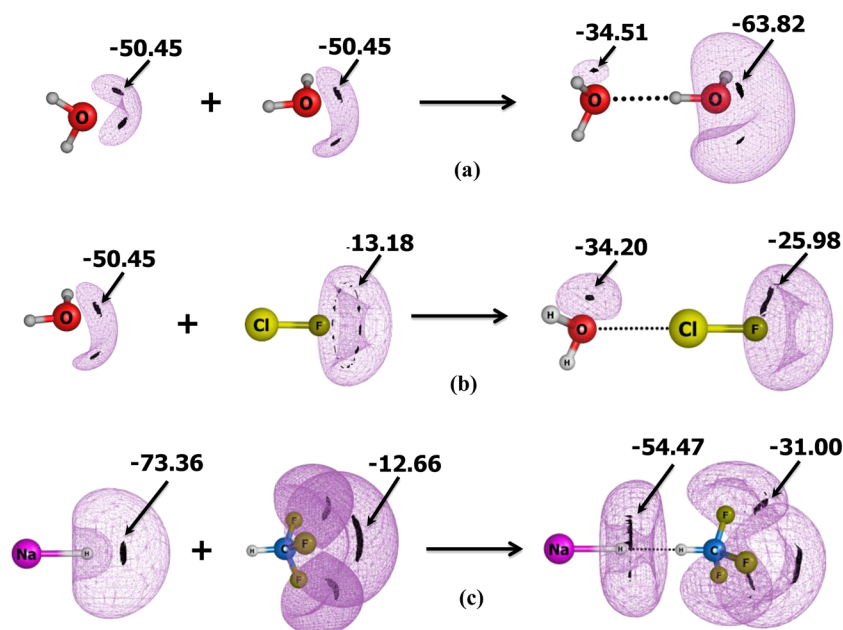
Figure 4. Change in V_{min} upon bond formation for (a) $H_2O...H_2O$, (b) $H_2O...ClF$, and (c) $NaH....HCF_3$. The black dots represent the location of the most negative MESP-valued point and the corresponding V_{min} values in kcal/mol are also depicted.

V_{min} is a (3, +3) critical point and the MESP value at this point is used as a sensitive descriptor to understand the flow of electron from one location to another location due to noncovalent binding. Since V_{min} measures the work done in brining a unit test positive charge from infinity to the location of the V_{min}, it is an energetic measure on the electrostatic influence. V_{min} is also related with the charge transfer by virtue of its relation to the continuous electron distribution (eq 1) and hence reflects the charge transfer taking place in the system due to noncovalent binding.

The electronic changes that accompany the bond formation can be clearly understood by comparing V_{min} values of isolated D and A molecules (designated as V_{min-A} and V_{min-D}, respectively) with V_{min} values of D and A molecules in the complex (designated as $V_{min-A'}$ and $V_{min-D'}$, respectively). Hence, the electronic reorganization during the bond formation can be quantified as $\Delta V_{min-D} = V_{min-D'} - V_{min-D}$ for donor and $\Delta V_{min-A} = V_{min-A'} - V_{min-A}$ for acceptor (Table 1). For all the complexes, ΔV_{min-D} is positive indicating the loss in electron density from D and ΔV_{min-A} is negative indicating gain in electron density by A. Thus, A becomes more electron rich at the expense of D meaning that the interaction between D and A can be best described as eDA interaction. To illustrate this point, MESP plots of a representative set of complexes are given in Figure 4 along with their V_{min} values. In the formation of H_2O dimer ($H_2O...H_2O$), one of the H_2O molecules (A) gains electron density at the expense of the other (D) (Figure 4a). In this case, V_{min-D} and $V_{min-D'}$ are -50.45 and -34.51 kcal/mol, respectively and V_{min-A} and $V_{min-A'}$ are -50.45 and -63.82 kcal/mol, respectively. ΔV_{min-A} and ΔV_{min-D} are 15.95 and -13.37 kcal/mol, respectively, which indicates that a significant amount of electron density of D has been transferred to A during the formation of the noncovalent complex. Another interesting observation is that the magnitude of ΔV_{min-A} depends on the electron donating ability of the D in D-A. For instance, in the case of C−H...Y systems $H_3N...HCCH$ and $H_2S...HCCH$, V_{min} value -22.29 kcal/mol of the isolated HCCH is changed to -32.38 kcal/mol for the former and -26.73 kcal/mol for the

latter, which accounts for the stronger electron donating power NH_3 (ΔV_{min-A} -10.09 kcal/mol) than H_2S (ΔV_{min-A} -4.44 kcal/mol). The ΔV_{min-A} of negatively charged systems are more negative than neutral ones, which indicate a greater shift of electron density toward the acceptor side. As the ΔV_{min-D} increases, the electron donation from D increases whereas a more negative ΔV_{min-A} indicates higher electron accepting power of A in D-A complex. This interpretation of ΔV_{min-D} and ΔV_{min-A} suggests that the quantity $\Delta\Delta V_{min} = \Delta V_{min-D} - \Delta V_{min-A}$ could be used as a measure of the donor−acceptor strength of the noncovalent interaction. A reasonably good linear correlation between $\Delta\Delta V_{min}$ and E_{nb} is obtained (Figure 5) that suggests that the strength of the noncovalent bond is directly related with the donor−acceptor strength.
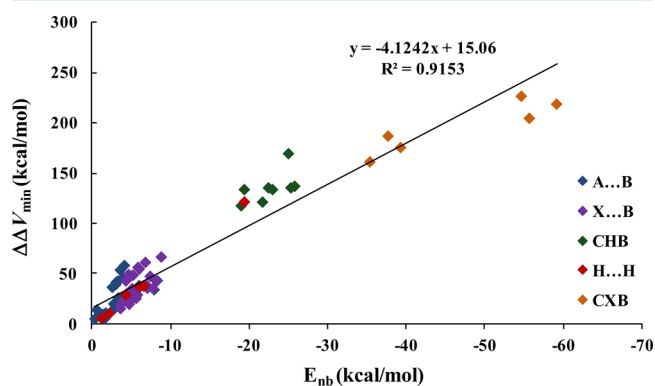

Figure 5. Linear relationship between $\Delta\Delta V_{min}$ and noncovalent interaction energy (E_{nb}).

The V_{min} approach to measure the donor−acceptor strength is not possible in some cases because of the absence of a local V_{min} in D or A of the D-A complex and such systems include $Ar...HCH_3$, $H_3P...H_2O$, $H_3P...H_2S$, $H_3...HF$, $H_3P...HCl$, $H_3N...ClF$, and all cationic systems. Further, being a sensitive spatial property, V_{min} can be affected by secondary interactions

from other parts of the molecule and this may be the reason for not finding a strong linear correlation between $\Delta\Delta V_{min}$ and E_{nb} ($R = 0.915$). On the other hand, the nucleus-centered quantity V_n is less sensitive to secondary interactions and all systems including cations show V_n. We have computed V_n at the donor (V_{n-D}) and acceptor (V_{n-A}) atoms in free molecules as well as V_n at the donor ($V_{n-D'}$) and acceptor atoms ($V_{n-A'}$) in complexes and determined the quantities $\Delta V_{n-A} = V_{n-A'} - V_{n-A}$ and $\Delta V_{n-D} = V_{n-D'} - V_{n-D}$ (Scheme 1 and Table 1). The quantities ΔV_{n-D}

Scheme 1. X-A Represents the Electron Acceptor and D-Z Represents the Electron Donor[a]

$$V_{n-A} \quad V_{n-D} \qquad\qquad V_{n-A'} \quad V_{n-D'}$$

$$\mathbf{X-A} + \mathbf{D-Z} \longrightarrow \mathbf{X-A} \text{-----} \mathbf{D-Z}$$
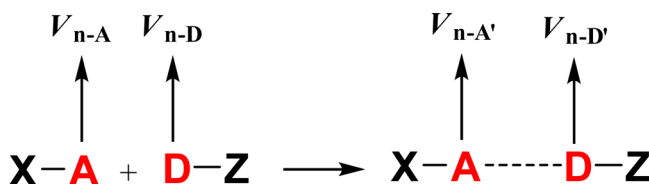
[a]D and A are the atoms participating in the donor–acceptor interaction. MESP at the nuclei are designated with symbols V_{n-A}, $V_{n-A'}$, V_{n-D} and $V_{n-D'}$.

and ΔV_{n-A} can be considered as electron donating ability and electron accepting ability of the acceptor and donor atoms, respectively. In all the A...B, X...B, CHB, CXB, and H...H type complexes, ΔV_{n-D} is positive and ΔV_{n-A} is negative indicating that D donates electron density to A during bond formation. This result is very similar to that obtained from V_{min} analysis and also means that $\Delta\Delta V_n = \Delta V_{n-D} - \Delta V_{n-A}$ could be used as a good descriptor to measure the donor–acceptor power of the D-A complex.

A single linear correlation exists between $\Delta\Delta V_n$ and E_{nb} for all the D-A complexes except the bridged ones as shown in Figure 6. This correlation has an R^2 value of 0.976 suggesting
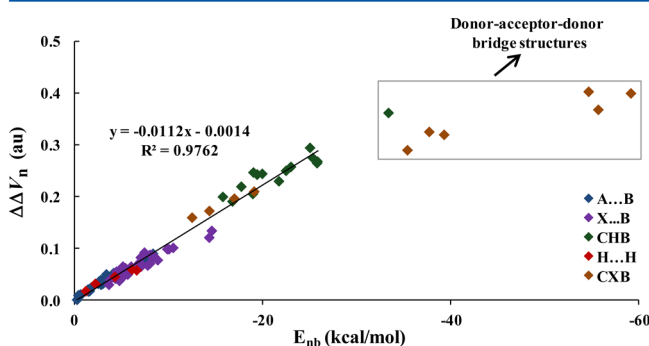

Figure 6. Linear relationship between $\Delta\Delta V_n$ and noncovalent interaction energy (E_{nb}).

that V_n can be effectively used for describing the bonding strength of all the D-A complexes irrespective of which category they belong to, viz. hydrogen bonds, halogen bonds, charge-assisted hydrogen bonds, charge-assisted halogen bonds, and dihydrogen bonds. The correlations of $\Delta\Delta V_{min}$ and $\Delta\Delta V_n$ with E_{nb} also suggest the dominance of electrostatic contribution to the total interaction energy of noncovalent complexes. The exclusion of the bridged systems (H_3O^+...H_2O, F^-...I...F, F^-...Br...F, Cl^-...I...F, Cl^-...Br...F, F^-...I...Br, and Cl^-...I...Br) from the linear correlation is justified because in such systems, the central atom show strong electron accepting interactions from two other atoms compared to only such interaction in

nonbridged structures. The electronic reorganization during the bond formation in bridged anionic CXB complexes is demonstrated by means of MESP plots in Figure 7. In F^-...IF complex, I is placed symmetrically with respect to both the F atoms making it difficult to distinguish which F atom is the electron donor. This suggests the possibility of a resonance combination of F^-...IF and F...IF^- and equal sharing of negative charge on both F atoms. Hence we may assume that central iodine accepts charge density from both the F atoms leading to a donor–acceptor–donor interaction in the bridged complex. This argument is further supported by the fact the both F atoms show the same V_{min} value in the complex (-158.20 kcal/mol) and a large enhancement in the negative MESP on the iodine atom (-110.63 kcal/mol). The MESP plot of F...IBr also suggests the electron accepting interaction of iodine with partially negatively charged F and Br atoms. Energy decomposition analysis (EDA) by Wolters and Bickelhaupt[65] has shown that halogen bonded trihalides of the type DX...A^- (D, X, A = F, Cl, Br, I) are generally associated with a weaker electrostatic attraction and a significantly strong covalent component arising from the stabilizing HOMO−LUMO interaction between the np-type lone pair on the halogen accepting fragment, A^- and the D-X antibonding σ^* LUMO on the halogen bond donating fragment DX.

The significance of the correlation between $\Delta\Delta V_n$ and E_{nb} is that the MESP approach unifies all kinds of hydrogen bonds, halogen bonds and dihydrogen bonds as eDA interactions. Hence, a hydrogen bond could be considered as an eDA interaction in which a hydrogen atom acts as an electron acceptor. This interpretation is also applicable for dihydrogen bonds. Similarly, a halogen bond may be defined as an eDA interaction in which a halogen atom acts as the electron acceptor.

CONCLUSIONS

High level ab initio calculations coupled with atoms-in-molecules (AIM) and molecular electrostatic potential (MESP) approaches have been used for the study of a variety of intermolecular hydrogen bonds, halogen bonds, and dihydrogen bonds to devise descriptor to quantify these noncovalent interactions. Although ρ-values prove to be effective within a homogeneous sample of D-A complexes where either the electron donor or acceptor is fixed, the applicability of these parameters for a heterogeneous sample of D-A complexes with different electron donors and/or acceptors is limited. An analysis of the V_{min} values of donor and acceptor molecules before and after complex formation shows that there is a considerable rearrangement of electron density within each monomer during the bond formation. A strong linear correlation is established between a parameter based on V_n viz. $\Delta\Delta V_n$ and E_{nb} of all the complexes. The molecular electrostatic potential at the nucleus emerges as an effective parameter to describe electron donor−acceptor interactions irrespective of the nature and strength of the interactions. To conclude, a hydrogen bond represents an eDA interaction in which a hydrogen atom acts as an electron acceptor whereas a halogen bond represents as an eDA interaction in which a halogen atom acts as the electron acceptor. We have also shown that charge-assisted bridged complexes belong to a new category of donor−acceptor−donor complexes.
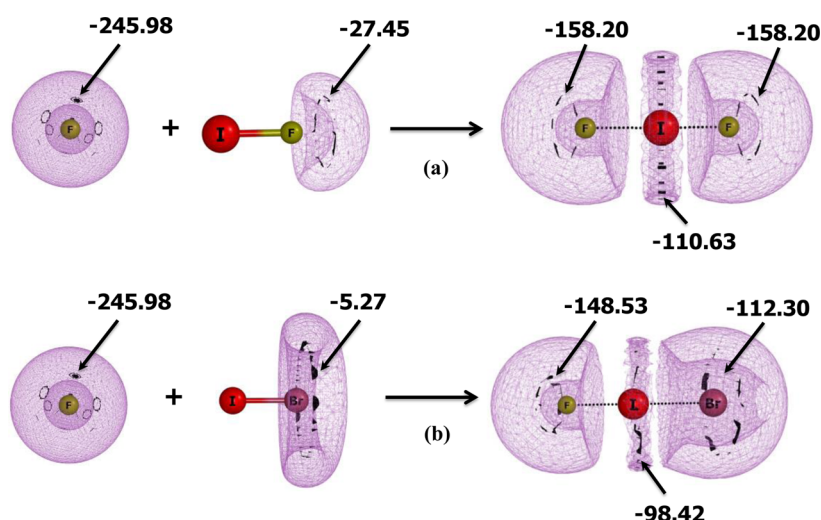
Figure 7. Change in V_{min} upon bond formation in electron donor−acceptor−donor complexes (a) F⁻...IF and (b) F⁻...IBr. The black dots represent the location of the most negative MESP-valued point and the corresponding V_{min} values in kcal/mol are also depicted.

■ ASSOCIATED CONTENT

⑤ Supporting Information

CCSD(T) benchmark values of energies and other supporting data mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ ABBREVIATIONS

MESP, molecular electrostatic potential; eDA, electron donor−acceptor; AIM, atoms in molecules

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