

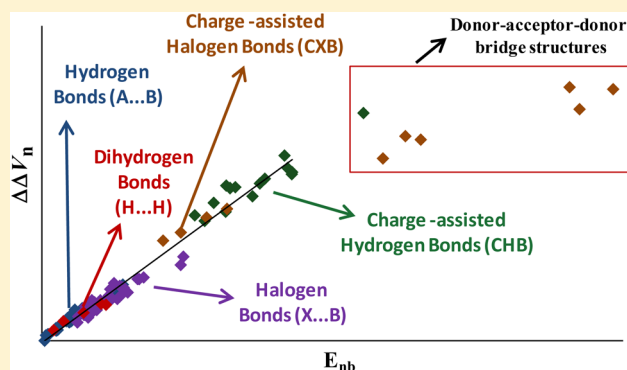
A Molecular Electrostatic Potential Analysis of Hydrogen, Halogen, and Dihydrogen Bonds

Neetha Mohan and Cherumuttathu H. Suresh*

Inorganic and Theoretical Chemistry Section, CSTD, CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum 695 019, India

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. Desiraju² 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 recommendations¹⁶ 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-workers²⁷ 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

Received: November 25, 2013

Revised: January 21, 2014

Published: February 7, 2014

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. Sathyamurthy⁴⁰ 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 theory⁵⁵ 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 nonvalent 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 Bernardi⁵⁶ counterpoise technique. Gaussian09⁵⁷ 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 \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 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 \mathbf{r} , the positive charges on the neighboring nuclei, and the electron density in closer vicinity of point \mathbf{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.

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

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.

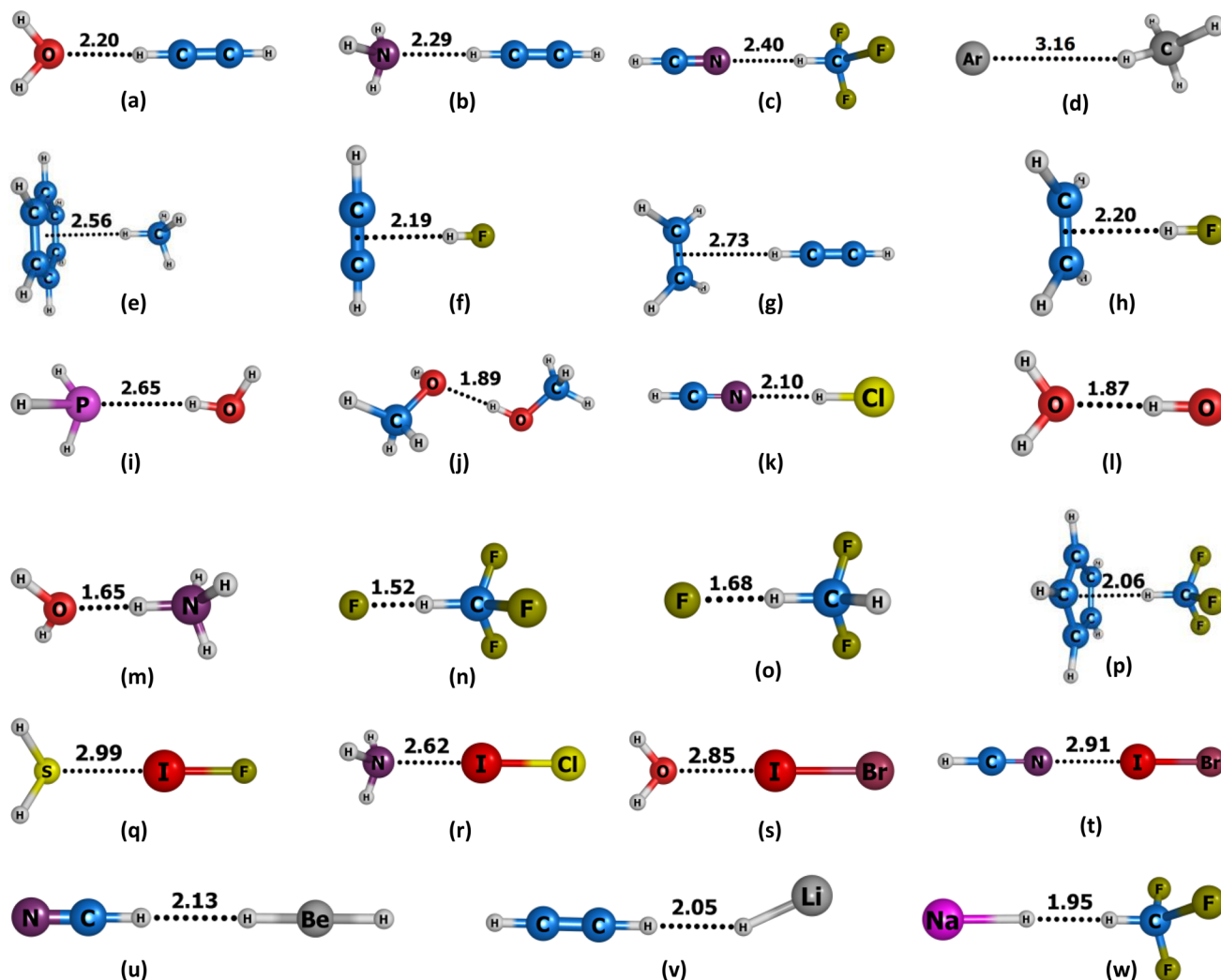


Figure 1. Representative set of intermolecular hydrogen and halogen bonded complexes studied: (a) $\text{H}_2\text{O} \cdots \text{HCCH}$, (b) $\text{H}_3\text{N} \cdots \text{HCCH}$, (c) $\text{HCN} \cdots \text{HCF}_3$, (d) $\text{Ar} \cdots \text{HCH}_3$, (e) $\text{H}_6\text{C}_6 \cdots \text{HCH}_3$, (f) $\text{H}_2\text{C}_2 \cdots \text{HF}$, (g) $\text{H}_4\text{C}_2 \cdots \text{HCCH}$, (h) $\text{H}_4\text{C}_2 \cdots \text{HF}$, (i) $\text{H}_3\text{P} \cdots \text{H}_2\text{O}$, (j) $\text{H}_3\text{CHO} \cdots \text{HOCH}_3$, (k) $\text{HCN} \cdots \text{HCl}$, (l) $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$, (m) $\text{H}_2\text{O} \cdots \text{H}_4^+\text{N}$, (n) $\text{F}^- \cdots \text{HCF}_3$, (o) $\text{F}^- \cdots \text{H}_2\text{CF}_2$, (p) $\text{H}_5\text{C}_5 \cdots \text{HCF}_3$, (q) $\text{H}_2\text{S} \cdots \text{IF}$, (r) $\text{H}_3\text{N} \cdots \text{ICl}$, (s) $\text{H}_2\text{O} \cdots \text{IBr}$, (t) $\text{HCN} \cdots \text{IBr}$, (u) $\text{HBeH} \cdots \text{HCN}$, (v) $\text{LiH} \cdots \text{HCCH}$, (w) $\text{NaH} \cdots \text{HCF}_3$. 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.

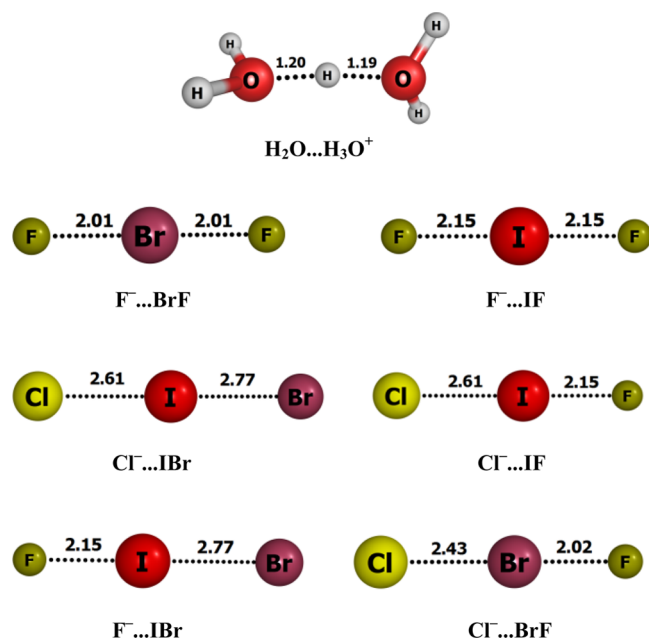
Table 1 presents the E_{nb} values of a representative set of complexes along with ρ and $\nabla^2\rho$ at bcp. The values of ρ and $\nabla^2\rho$ for $\text{H} \cdots \text{H}$ and most of the $\text{A} \cdots \text{B}$ complexes fall in the typical range⁴³ proposed for ρ (0.002–0.035 au) and $\nabla^2\rho$ (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 $\text{H}_3\text{O}^+ \cdots \text{H}_2\text{O}$, all other D-A systems exhibit typical closed-shell interactions by virtue of their positive $\nabla^2\rho$ values. $\text{H}_3\text{O}^+ \cdots \text{H}_2\text{O}$ corresponds to a Zundel ion⁶⁴ and have a $\nabla^2\rho$ value of -0.564 au, which is characteristic of a bond with covalent nature. Anionic CXB complexes *viz.* $\text{F}^- \cdots \text{IF}$, $\text{F}^- \cdots \text{BrF}$, $\text{Cl}^- \cdots \text{IF}$, $\text{Cl}^- \cdots \text{BrF}$, $\text{F}^- \cdots \text{IBr}$, and $\text{Cl}^- \cdots \text{IBr}$ 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 $\text{F}^- \cdots \text{IF}$ the position of I is symmetric with respect to both the F atoms meaning that the complex is a resonance combination of $\text{F}^- \cdots \text{IF}$ and $\text{F} \cdots \text{IF}^-$. Similar bonding scenario is seen in $\text{F}^- \cdots \text{BrF}$, $\text{Cl}^- \cdots \text{IF}$, $\text{Cl}^- \cdots \text{BrF}$, $\text{F}^- \cdots \text{IBr}$, and $\text{Cl}^- \cdots \text{IBr}$. The cationic complex $\text{H}_3\text{O}^+ \cdots \text{H}_2\text{O}$ also exhibits a bridged configuration ($\text{H}_2\text{O} \cdots \text{H}^+ \cdots \text{OH}_2$) with the H^+ placed at 1.19 and 1.20 Å from each of the two H_2O molecules (Figure 2).

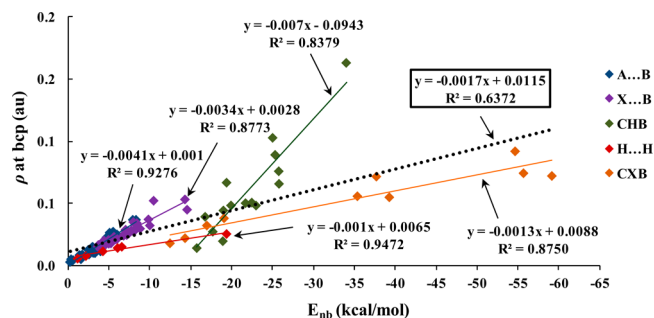
It is well established that the topological parameters at bcp correlate with E_{nb} for a variety of noncovalent complexes. Sathiyamurthi et al.⁴⁰ showed a linear relationship between ρ and E_{nb} as well as $\nabla^2\rho$ and E_{nb} for a set of intermolecular complexes of varying strengths ranging 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 ($\text{A} \cdots \text{B}$), halogen-bonded ($\text{X} \cdots \text{B}$), dihydrogen-bonded ($\text{H} \cdots \text{H}$), charge-assisted hydro-

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

complex	E_{nb} (kcal/mol)	ρ (au)	$\nabla^2\rho$ (au)	$\Delta V_{\text{min-A}}$ (kcal/mol)	$\Delta V_{\text{min-D}}$ (kcal/mol)	$\Delta\Delta V_{\text{min}}$ (kcal/mol)	$\Delta V_{\text{n-A}}$ (au)	$\Delta V_{\text{n-D}}$ (au)	$\Delta\Delta V_{\text{n}}$ (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
H ₃ P...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.

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

**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.

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.

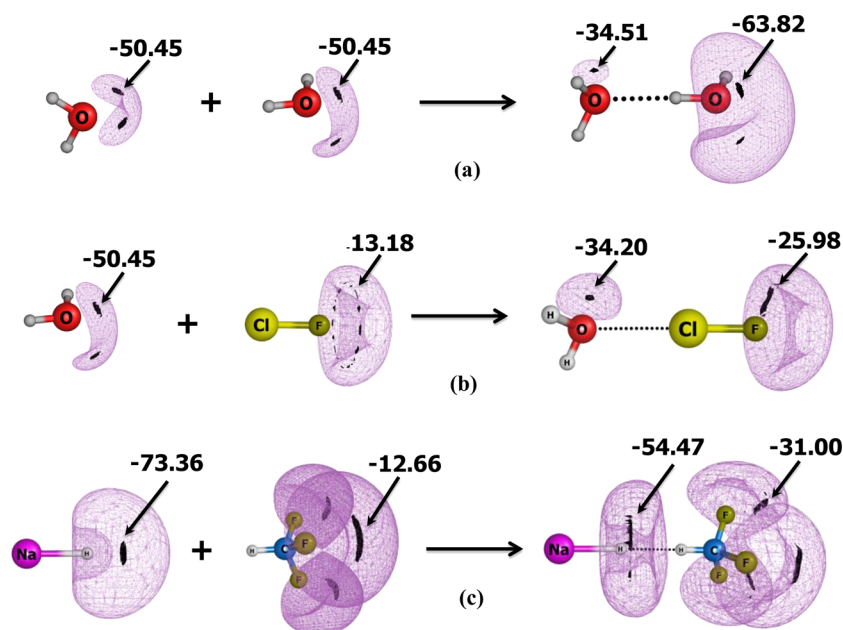


Figure 4. Change in V_{\min} upon bond formation for (a) $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$, (b) $\text{H}_2\text{O} \cdots \text{ClF}$, and (c) $\text{NaH} \cdots \text{HCF}_3$. The black dots represent the location of the most negative MESP-valued point and the corresponding V_{\min} values 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 bringing 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, $\Delta V_{\min-D}$ is positive indicating the loss in electron density from D and $\Delta V_{\min-A}$ 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 ($\text{H}_2\text{O} \cdots \text{H}_2\text{O}$), 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. $\Delta V_{\min-A}$ and $\Delta V_{\min-D}$ 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 $\Delta V_{\min-A}$ depends on the electron donating ability of the D in D-A. For instance, in the case of C-H...Y systems $\text{H}_3\text{N} \cdots \text{HCCH}$ and $\text{H}_2\text{S} \cdots \text{HCCH}$, 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 ($\Delta V_{\min-A}$ -10.09 kcal/mol) than H_2S ($\Delta V_{\min-A}$ -4.44 kcal/mol). The $\Delta V_{\min-A}$ of negatively charged systems are more negative than neutral ones, which indicate a greater shift of electron density toward the acceptor side. As the $\Delta V_{\min-D}$ increases, the electron donation from D increases whereas a more negative $\Delta V_{\min-A}$ indicates higher electron accepting power of A in D-A complex. This interpretation of $\Delta V_{\min-D}$ and $\Delta V_{\min-A}$ 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.

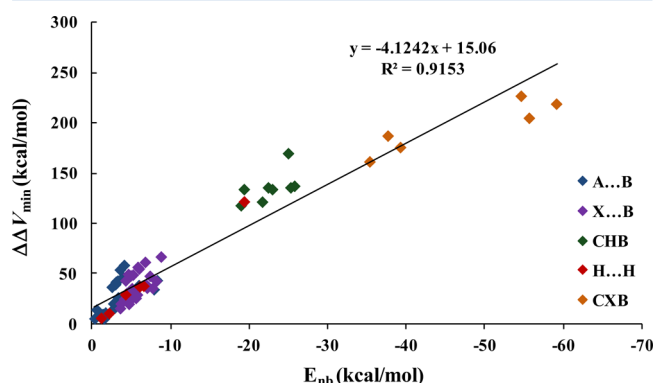
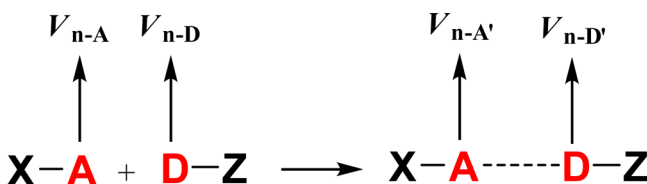


Figure 5. Linear relationship between $\Delta\Delta V_{\min}$ and noncovalent interaction energy (E_{nb}).

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 $\text{Ar} \cdots \text{HCH}_3$, $\text{H}_3\text{P} \cdots \text{H}_2\text{O}$, $\text{H}_3\text{P} \cdots \text{H}_2\text{S}$, $\text{H}_3 \cdots \text{HF}$, $\text{H}_3\text{P} \cdots \text{HCl}$, $\text{H}_3\text{N} \cdots \text{ClF}$, 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



^aD 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

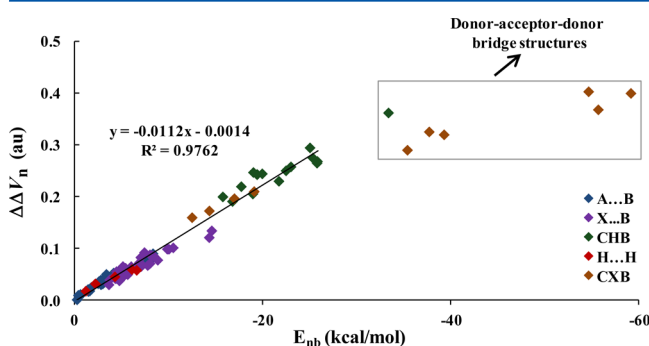


Figure 6. Linear relationship between $\Delta\Delta V_n$ and noncovalent interaction energy (E_{nb}).

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 ($\text{H}_3\text{O}^+\cdots\text{H}_2\text{O}$, $\text{F}^-\cdots\text{I}\cdots\text{F}$, $\text{F}^-\cdots\text{Br}\cdots\text{F}$, $\text{Cl}^-\cdots\text{I}\cdots\text{F}$, $\text{Cl}^-\cdots\text{Br}\cdots\text{F}$, $\text{F}^-\cdots\text{I}\cdots\text{Br}$, and $\text{Cl}^-\cdots\text{I}\cdots\text{Br}$) from the linear correlation is justified because in such systems, the central atom shows 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 $\text{F}^-\cdots\text{I}\cdots\text{F}$ 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 $\text{F}^-\cdots\text{I}\cdots\text{F}$ and $\text{F}\cdots\text{I}\cdots\text{F}^-$ 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 $\text{F}\cdots\text{I}\cdots\text{Br}$ also suggests the electron accepting interaction of iodine with partially negatively charged F and Br atoms. Energy decomposition analysis (EDA) by Wolters and Bickelhaupt⁶⁵ has shown that halogen bonded trihalides of the type $\text{DX}\cdots\text{A}^-$ (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.

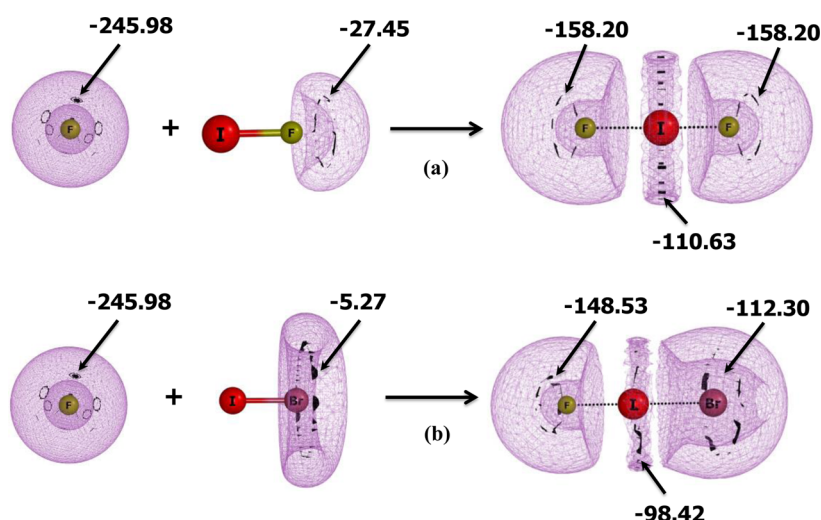


Figure 7. Change in V_{\min} upon bond formation in electron donor–acceptor–donor complexes (a) $\text{F}^- \cdots \text{IF}$ and (b) $\text{F}^- \cdots \text{IBr}$. The black dots represent the location of the most negative MESP-valued point and the corresponding V_{\min} values in kcal/mol are also depicted.

■ ASSOCIATED CONTENT

■ 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>.

■ AUTHOR INFORMATION

Corresponding Author

*Email: sureshch@gmail.com.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research work is supported by the Council of Scientific and Industrial Research (CSIR), Government of India, through a project CSC0129. N.M. is thankful to CSIR for providing a senior research fellowship.

■ ABBREVIATIONS

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

■ REFERENCES

- (1) Buckingham, A. D.; Fowler, P. W.; Hutson, J. M. Theoretical Studies of Van der Waals Molecules and Intermolecular Forces. *Chem. Rev.* **1988**, *88*, 963–988.
- (2) Desiraju, G. R. Hydrogen Bridges in Crystal Engineering: Interactions without Borders. *Acc. Chem. Res.* **2002**, *35*, 565–573.
- (3) Gilli, G.; Gilli, P. Towards an Unified Hydrogen-Bond Theory. *J. Mol. Struct.* **2000**, *552*, 1–15.
- (4) Gilli, G.; Gilli, P. *The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory*; Oxford University Press: New York, 2009.
- (5) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. Covalent Nature of the Strong Homonuclear Hydrogen Bond. Study of the O–H–O System by Crystal Structure Correlation Methods. *J. Am. Chem. Soc.* **1994**, *116*, 909–915.
- (6) Gotch, A. J.; Zwier, T. S. The Spectroscopy and Dynamics of π -Hydrogen-Bonded Complexes: Benzene–HCl/DCl and Toluene–HCl/DCl. *J. Chem. Phys.* **1990**, *93*, 6977–6987.
- (7) Grabowski, S. J. Ab Initio Calculations on Conventional and Unconventional Hydrogen Bonds—Study of the Hydrogen Bond Strength. *J. Phys. Chem. A* **2001**, *105*, 10739–10746.
- (8) Grabowski, S. J. Hydrogen Bonding Strength - Measures Based on Geometric and Topological Parameters. *J. Phys. Org. Chem.* **2004**, *17*, 18–31.
- (9) Grabowski, S. J. What is the Covalency of Hydrogen Bonding? *Chem. Rev.* **2011**, *111*, 2597–2625.
- (10) Kollman, P.; McKelvey, J.; Johansson, A.; Rothenberg, S. Theoretical Studies of Hydrogen-Bonded Dimers. Complexes Involving HF, H₂O, NH₃, HCl, H₂S, PH₃, HCN, HNC, HCP, CH₂NH, H₂CS, H₂CO, CH₄, CF₃H, C₂H₂, C₂H₄, C₆H₆, F[−], and H₃O⁺. *J. Am. Chem. Soc.* **1975**, *97*, 955–965.
- (11) Morokuma, K. Why Do Molecules Interact? The Origin of Electron Donor–Acceptor Complexes, Hydrogen Bonding, and Proton Affinity. *Acc. Chem. Res.* **1977**, *10*, 294–300.
- (12) Müller-Dethlefs, K.; Hobza, P. Noncovalent Interactions: A Challenge for Experiment and Theory. *Chem. Rev.* **2000**, *100*, 143–168.
- (13) Desiraju, G. R. A Bond by Any Other Name. *Angew. Chem., Int. Ed.* **2011**, *50*, 52–59.
- (14) Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J. Defining the Hydrogen Bond: An Account (IUPAC Technical Report). *Pure Appl. Chem.* **2011**, *83*, 1619–1636.
- (15) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, 1997.
- (16) Desiraju, G. R.; Ho, P. S.; Legon, A. C.; Marquardt, R.; Metrangola, P.; Politzer, P. A.; Resnati, G.; Rissanen, K. Definition of the Halogen Bond. *Pure Appl. Chem.* **2013**, *85*, 1711–1713.
- (17) Brinck, T.; Murray, J. S.; Politzer, P. Surface Electrostatic Potentials of Halogenated Methanes as Indicators of Directional Intermolecular Interactions. *Int. J. Quantum Chem.* **1992**, *44*, 57–64.
- (18) Brinck, T.; Murray, J. S.; Politzer, P. Molecular Surface Electrostatic Potentials and Local Ionization Energies of Group V–VII Hydrides and their Anions: Relationships for Aqueous and Gas-Phase Acidities. *Int. J. Quantum Chem.* **1993**, *48*, 73–88.
- (19) Murray, J. S.; Paulsen, K.; Politzer, P. Molecular Surface Electrostatic Potentials in the Analysis of Non-Hydrogen-Bonding Noncovalent Interactions. *Proc. - Indian Acad. Sci., Chem. Sci.* **1994**, *106*, 267–275.

- (20) Clark, T.; Hennemann, M.; Murray, J. S.; Politzer, P. Halogen Bonding: The σ -Hole. *J. Mol. Model.* **2007**, *13*, 291–296.
- (21) Politzer, P.; Murray, J. S.; Clark, T. Halogen Bonding and Other σ -Hole Interactions: A Perspective. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11178–11189.
- (22) Kovács, A.; Varga, Z. Halogen Acceptors in Hydrogen Bonding. *Coord. Chem. Rev.* **2006**, *250*, 710–727.
- (23) Legon, A. C. Prereactive Complexes of Dihalogens XY with Lewis Bases B in the Gas Phase: A Systematic Case for the Halogen Analogue B...XY of the Hydrogen Bond B...HX. *Angew. Chem., Int. Ed.* **1999**, *38*, 2686–2714.
- (24) Desiraju, G. R.; Parthasarathy, R. The Nature of Halogen...Halogen Interactions: Are Short Halogen Contacts Due to Specific Attractive Forces or Due to Close Packing of Nonspherical Atoms? *J. Am. Chem. Soc.* **1989**, *111*, 8725–8726.
- (25) Legon, A. C. π -Electron 'Donor-Acceptor' Complexes B...ClF and the Existence of the 'Chlorine Bond'. *Chem.—Eur. J.* **1998**, *4*, 1890–1897.
- (26) Bent, H. A. Structural Chemistry of Donor-Acceptor Interactions. *Chem. Rev.* **1968**, *68*, 587–648.
- (27) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. A New Intermolecular Interaction: Unconventional Hydrogen Bonds with Element-Hydride Bonds as Proton Acceptor. *Acc. Chem. Res.* **1996**, *29*, 348–354.
- (28) Ratajczak, H.; Orville-Thomas, W. J. *Molecular Interactions*; John Wiley & Sons: Chichester, 1980; Vol. 1.
- (29) Mulliken, R. S.; Person, W. B. *Molecular Complexes: A Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969.
- (30) Jonas, V.; Frenking, G.; Reetz, M. T. Comparative Theoretical Study of Lewis Acid-Base Complexes of BH_3 , BF_3 , BCl_3 , AlCl_3 , and SO_2 . *J. Am. Chem. Soc.* **1994**, *116*, 8141–8753.
- (31) Bader, R. F. W. A Quantum Theory of Molecular Structure and Its Applications. *Chem. Rev.* **1991**, *91*, 893–928.
- (32) Bader, R. F. W. Atoms in Molecules. *Acc. Chem. Res.* **1985**, *18*, 9–15.
- (33) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.
- (34) Pullman, B. A Lucid Introduction to Biological Applications of Mesp. *Int. J. Quantum Chem. Quantum Biol. Symp.* **1990**, *17*, 609.
- (35) Sjöberg, P.; Politzer, P. Use of the Electrostatic Potential at the Molecular Surface to Interpret and Predict Nucleophilic Processes. *J. Phys. Chem.* **1990**, *94*, 3959–3961.
- (36) Politzer, P.; Laurence, P. R.; Jayasuriya, K. Molecular Electrostatic Potentials: An Effective Tool for the Elucidation of Biochemical Phenomena. *Environ. Health Perspect.* **1985**, *61*, 191–202.
- (37) Sen, K. D.; Politzer, P. Characteristic Features of the Electrostatic Potentials of Singly Negative Monoatomic Ions. *J. Chem. Phys.* **1989**, *90*, 4370–4372.
- (38) Knop, O.; Rankin, K. N.; Boyd, R. J. Coming to Grips with N-H...N Bonds. 2. Homocorrelations between Parameters Deriving from the Electron Density at the Bond Critical Point. *J. Phys. Chem. A* **2003**, *107*, 272–284.
- (39) Suresh, C. H.; Mohan, N.; Vijayalakshmi, K. P.; George, R.; Mathew, J. M. Typical Aromatic Noncovalent Interactions in Proteins: A Theoretical Study Using Phenylalanine. *J. Comput. Chem.* **2009**, *30*, 1392–1404.
- (40) Parthasarathi, R.; Subramanian, V.; Sathiyamurthy, N. Hydrogen Bonding without Borders: An Atoms-in-Molecules Perspective. *J. Phys. Chem. A* **2006**, *110*, 3349–3351.
- (41) Popelier, P. L. A.; Logothetis, G. Characterization of an Agostic Bond on the Basis of the Electron Density. *J. Organomet. Chem.* **1998**, *555*, 101–111.
- (42) Popelier, P. L. A. Characterization of a Dihydrogen Bond on the Basis of the Electron Density. *J. Phys. Chem. A* **1998**, *102*, 1873–1878.
- (43) Koch, U.; Popelier, P. L. A. Characterization of C–H–O Hydrogen Bonds on the Basis of the Charge Density. *J. Phys. Chem.* **1995**, *99*, 9747–9754.
- (44) Suresh, C. H.; Gadre, S. R. Electrostatic Potential Minimum of the Aromatic Ring as a Measure of Substituent Constant. *J. Phys. Chem. A* **2007**, *111*, 710–714.
- (45) Mathew, J.; Suresh, C. H. Use of Molecular Electrostatic Potential at the Carbene Carbon as a Simple and Efficient Electronic Parameter of N-Heterocyclic Carbenes. *Inorg. Chem.* **2010**, *49*, 4665–4669.
- (46) Gadre, S. R.; Bhadane, P. K. Patterns in Hydrogen Bonding Via Electrostatic Potential Topography. *J. Chem. Phys.* **1997**, *107*, 5625–5627.
- (47) Galabov, B.; Bobadova-Parvanova, P. Molecular Electrostatic Potential as Reactivity Index in Hydrogen Bonding: Ab Initio Molecular Orbital Study of Complexes of Nitrile and Carbonyl Compounds with Hydrogen Fluoride. *J. Phys. Chem. A* **1999**, *103*, 6793–6799.
- (48) Leroy, G.; Louterman-Leloup, G.; Ruelle, P. Contribution to the Theoretical Study of the Hydrogen Bond-I. *Bull. Soc. Chim. Belg.* **1976**, *85*, 205–218.
- (49) Politzer, P.; Murray, J. S. Molecular Electrostatic Potentials and Chemical Reactivity. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1991; Vol. 2.
- (50) Bobadova-Parvanova, P.; Galabov, B. Ab Initio Molecular-Orbital Study of Hydrogen-Bonded Complexes of Carbonyl Aliphatic Compounds and Hydrogen Fluoride. *J. Phys. Chem. A* **1998**, *102*, 1815–1819.
- (51) Gadre, S. R.; Pundlik, S. S. Complementary Electrostatics for the Study of DNA Base-Pair Interactions. *J. Phys. Chem. B* **1997**, *101*, 3298–3303.
- (52) Galabov, B.; Bobadova-Parvanova, P.; Ilieva, S.; Dimitrova, V. The Electrostatic Potential at Atomic Sites as a Reactivity Index in the Hydrogen Bond Formation. *J. Mol. Struct. THEOCHEM* **2003**, *630*, 101–112.
- (53) Dimitrova, V.; Ilieva, S.; Galabov, B. Electrostatic Potential at Atomic Sites as a Reactivity Descriptor for Hydrogen Bonding. Complexes of Monosubstituted Acetylenes and Ammonia. *J. Phys. Chem. A* **2002**, *106*, 11801–11805.
- (54) Dimitrova, V.; Ilieva, S.; Galabov, B. Electrostatic Potential at Nuclei as a Reactivity Index in Hydrogen Bond Formation. Complexes of Ammonia with C–H, N–H and O–H Proton Donor Molecules. *J. Mol. Struct. THEOCHEM* **2003**, *637*, 73–80.
- (55) Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618–622.
- (56) Boys, S. F.; Bernardi, F. The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, *19*, 553–566.
- (57) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2010.
- (58) Biegler-König, F.; Schönbohm, J.; Bayles, D. AIM2000 - A Program to Analyze and Visualize Atoms in Molecules. *J. Comput. Chem.* **2001**, *22*, 545–559.
- (59) Biegler-König, F.; Schönbohm, J. An Update to the AIM2000 - Program for Atoms in Molecules. *J. Comput. Chem.* **2002**, *23*, 1489–1494.

- (60) Politzer, P.; Truhlar, D. G. *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Plenum Press: New York, 1981.
- (61) Gadre, S. R.; Shirsat, R. N. *Electrostatics of Atoms and Molecules*; Universities Press: Hyderabad, India, 2000.
- (62) Madsen, G. K. H.; Iversen, B. B.; Larsen, F. K.; Kapon, M.; Reisner, G. M.; Herbststein, F. H. Topological Analysis of the Charge Density in Short Intramolecular O-H...O Hydrogen Bonds. Very Low Temperature X-Ray and Neutron Diffraction Study of Benzoylacetone. *J. Am. Chem. Soc.* **1998**, *120*, 10040–10045.
- (63) Schiøtt, B.; Iversen, B. B.; Madsen, G. K. H.; Bruice, T. C. Characterization of the Short Strong Hydrogen Bond in Benzoylacetone by Ab Initio Calculations and Accurate Diffraction Experiments. Implications for the Electronic Nature of Low-Barrier Hydrogen Bonds in Enzymatic Reactions. *J. Am. Chem. Soc.* **1998**, *120*, 12117–12124.
- (64) Schuster, P.; Zundel, G.; Sandorfy, C. *The Hydrogen Bond: Recent Developments in Theory and Experiments*; North-Holland Pub. Co.: Amsterdam, 1976.
- (65) Wolters, L. P.; Bickelhaupt, F. M. Halogen Bonding Versus Hydrogen Bonding: A Molecular Orbital Perspective. *ChemistryOpen* **2012**, *1*, 96–105.