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Hydrogen Bonding, Halogen Bonding and Lithium Bonding: An Atoms in Molecules and Natural Bond Orbital Perspective Towards Conservation of Total Bond Order, Inter- and Intra-molecular

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One hundred complexes have been investigated exhibiting D-X•••A interactions, where X = H, Cl or Li and DX is the 'X bond' donor and A is the acceptor. The optimized structures of all these complexes have been used to propose a generalized 'Legon-Millen rule' for the angular geometry in all these interactions. A detailed Atoms in Molecules (AIM) theoretical analysis confirms an important conclusion, known in the literature: there is a strong correlation between the electron density at the X•••A bond critical point (BCP) and the interaction energy for all these interactions. In addition, we show that extrapolation of the fitted line leads towards the ionic bond for Li-bonding (electrostatic) while for hydrogen and chlorine bonding, they lead toward the covalent bond. Further, we observe a strong correlation between the change in electron density at the D-X BCP and that at the X•••A BCP, suggesting a conservation of a bond order. The correlation found between penetration and electron density at BCP can be very useful for crystal structure analysis, which relies on arbitrary van der Waals radii for estimating penetration. Various criteria proposed for shared- and closed-shell interactions based on electron density topology have been tested for H/Cl/Li bonded complexes. Finally, using the natural bond orbital (NBO) analysis it is shown that the D-X bond weakens on X bond formation, whether it is ionic (DLi) or covalent (DH/DCl) and the respective indices, such as ionicity or covalent bond order decrease. Clearly, one can think of a conservation of bond order that includes ionic and covalent contributions to both D-X and X•••A bonds, for not only X = H/Cl/Li investigated here but also any atom involved in intermolecular bonding.

Introduction

Due to the unquestionable importance of hydrogen bonding to life as we know it, there have been an enormous interest in it, with several books being published in the last five decades [1–7]. Hydrogen bonding perhaps belongs to the general non-covalent interactions which are significantly weaker than a typical chemical bond (presumed to be covalent)[8,9]. Though, characterization, classification, properties and usefulness of these weak interactions have been actively investigated in the last two decades, such weak interactions are not new. A flavour of such interactions was given by Benesi and Hildebrand[10] as charge-transfer bonds first and later Mulliken[11] termed, complexes formed by weak interaction as electron donor-acceptor complexes and classified as outer and inner type complexes on the basis of strength of intermolecular interaction. The unique position of hydrogen in the periodic table, naturally led to studies on lithium bonding[12] and halogen bonding[13]. Legon[13], in his recent review used pre-reactive complexes which are mostly Mulliken's outer type complexes and described the rules for predicting the angular geometry for hydrogen and halogen bonds. The term 'Halogen bond' was used by Hassel in his Nobel lecture[14]. Recently it has been shown that halogen bonds can be orthogonal to hydrogen bonds in biomolecules (DNA), both playing crucial roles.[15]

Our group had earlier looked at a few selected D-X•••A complexes with DX = FH, FCl or FLi and A being four diverse acceptors, H_2O with lone pairs, C_2H_4 with a π pair, CH_3 with an unpaired electron and H_2 with a σ pair of electrons[16]. All these complexes had linear D-X•••A geometry. Many of the electron density topological properties calculated using Atoms in Molecules theory[17], suggested by Koch and Popelier[18] for C-H•••O hydrogen bonding, were comparable for the three different interactions. There was a strong correlation between electron density at the X•••A bond critical point and the interactions energy, though the four acceptors were very different. However, it was noted that the slopes of these correlation plots were very similar for X = H and Cl (263 and 277 respectively) and that for X = Li was distinctly different (769). The sign of the Laplacian indicated that all are closed shell (non-covalent) interactions. We were curious to see if this trend is general or if it was only applicable for the limited set of complexes chosen for the study. Since our work, detailed AIM theoretical analysis has been reported for halogen bonding [19] and lithium bonding [20]. Our main objective in this work is to take a comprehensive look at all these three interactions with a large number of examples and identify similarities and differences.

Though, the term non-covalent interaction has gained popularity[8], there have been discussions about the extent of covalent contribution to hydrogen bonding from the early days[1–7]. Hydrogen bonding has contributions from electrostatics, polarization, dispersion forces, and charge-transfer covalency to varying extents. The covalent contribution to hydrogen bonding was confirmed by NMR[21] and Compton scattering[22] experiments, published around the same time in 1999 and is now generally accepted. The recent IUPAC recommendation on the definition of hydrogen bonding emphasizes on the 'evidence for bond formation'[23] and Grabowski has reviewed 'the covalency in hydrogen bonding'[24]. Even more recently, visualisation of hydrogen bonding has been made possible by non-contact atomic force microscopy[25]. Hydrogen bonding was initially assumed to be 'simple electrostatic interaction' between two dipoles leading Huggins to suggest the term 'hydrogen bridge'[26]. Hydrogen bonding is still described as 'just electrostatic interaction between two dipoles' in some sources.[27] Unwillingness to accept the term 'hydrogen bond' appears to come out of the conviction that a chemical bond has to be covalent (shared shell interaction). It is surprising as 'ionic bonding' (closed-shell interaction) is always taught along with 'covalent bonding' starting from high school chemistry.

Both AIM[28,17] and NBO[29] theoretical methods have been extensively used to investigate hydrogen bonds, halogen bonds and lithium bonds. Several criteria based on AIM have been suggested to distinguish between closed-shell and shared-shell interactions. These criteria have been examined comprehensively in this work for H/Cl/Li-bonding. Our results clearly indicate that the complexes with X = H and Cl are very similar with the nature of interaction varying from closed shell (ionic/electrostatic) to shared shell (covalency). All D-Li•••A complexes have mostly closed shell interactions with a very small non-zero covalent contribution. This comprehensive study has revealed one important conclusion to us. It is time now to think about a conservation of a total bond order that includes covalency and ionicity in both inter- and intra-molecular bonding. Conservation of bond order is a concept that has been around from the time of Pauling.[7] Detailed comparison between what is proposed here and some results from earlier work is given towards the end of this manuscript.

Computational Details

All the 100 complexes investigated in this work can be written in short as D-X•••A, representing the bond donor group X-D and an acceptor group A which has lone pair(s) of electrons (H_2O, NH_3), σ-electrons (H_2), π-electrons (C_2H_4,C_2H_2) or unpaired electron (CH_3). In the donor part X-D, D = CN, NC, CCH, H, F, Cl, Br or OH and X = H, Li or Cl. Out of these 100 complexes, 40, 35 and 25 are the examples of lithium, hydrogen and chlorine bonding respectively. All the structures were optimized at MP2(full)[30] (second-order Møller-Plesset perturbation theory) level of theory which does not assume a frozen core. The Dunning[31] basis set used for this level of theory is aug-cc-PVTZ (augmented correlation-consistent polarized valence triple-zeta basis set). In our experience, MP2(full)/aug-cc-PVTZ level of calculations offer the right balance in terms of both reliability and speed considering the large number of complexes investigated. Calculations have been performed using Gaussian09 and Gaussian03 suite of programs[32]. Frequency calculations were performed at the same level of theory and basis set for all complexes in order to confirm that the obtained structures correspond to true energy minima. The binding energy of the complex is calculated as the difference between complex energy and the sum of the monomers energies i.e. supermolecule approach. For the correction of interaction energy from the inherent basis set superposition error (BSSE), counterpoise (CP) method[33] was used for all complexes.

The atoms in molecules (AIM) theory[17] has been used to analyze the topology of all the optimized complexes with the help of AIMALL[34] and AIM2000[35] programs. Natural resonance theory (NRT)[36], an inbuilt function in NBO6.0[37] program has been used to calculate the fraction of covalency and ionicity for X-D and A•••X bond.

Results and Discussion

The BSSE corrected binding energies and geometrical parameters of all the systems at MP2(full)/aug-cc-PVTZ are presented in Table 1, where *d(A•••X)* and *d(X-D)* define the bond lengths between A and X and X and D, respectively. The X bond angle has been denoted as *θ(A•••X-D)*. All the distances are in Å and energies in kJ/mol. The bond elongation represents the increase in bond length of X-D after complex formation. The complexes considered in this work could have other minima but this work focuses on the 'X-bonded' structures having *θ* close to 180°.

Structure: Generalized Legon-Millen Rule for Angular Geometry

Legon and Millen suggested rules for predicting the angular geometry of A•••H-D hydrogen bonded complexes[13]. Their rules were suggested for hydrogen bonded complexes with lone pair (Rule 1) or π pair of electrons (Rule 2) as hydrogen bond acceptors. A close inspection of the results in Table 1 indicates that these are applicable for all the complexes investigated in this work. However, Table 1 summarizes typical structural parameters reported in the literature focusing on the A•••X-D. Indeed, when A is NH_3, C_2H_4, C_2H_2, H_2 or CH_3, the two distances and one angle are sufficient to see if Legon-Millen rules work. It may be noted that the acceptors have been expanded to include σ bonded and unpaired electrons as well. One can anticipate complications for hydrogen bonded complexes with H_2O as acceptor as discussed below.

Water has two lone pairs of electrons which are commonly mistaken to be degenerate arising from sp^3 hybridization of the O atom. However, an isolated H_2O molecule should obey the symmetry rules for C_{2v} point group and has two non-degenerate orbitals, one in the plane of H_2O and one perpendicular to the plane. Hence DX could approach O atom in two directions. One is perpendicular to the plane of H_2O the X•••O line making an angle of 90° with the C_2 axis of H_2O and the other is along the C_2 axis in the direction opposite to the two H atoms. Thus, in principle, complexes involving H_2O as acceptors could have two geometrical isomers. However, as of now there is no experimental or theoretical evidence for this and only one structure has been found for these complexes which have H_2O as acceptor. A close examination of the direction in which DX approaches H_2O indicates that they have no obvious relations to the lone pair directionality in the monomer. The angle between D-X line and C_2 axis of H_2O varies widely. For example, in H_2O•••HCN it is 180° but in H_2O•••H_2O it is 118° (See Table 1). Interestingly, all the H_2O•••LiD complexes have this angle as 180° except for H_2O•••LiCl. One could conclude that H_2O•••HCN and H_2O•••LiD structures are dominated by electrostatics and the two dipoles have aligned in a head to tail fashion. However, as shown later, NBO analysis does show partial covalency in all complexes including Li-bonded ones.

Despite the complexity pointed above, all these complexes have O•••HD nearly linear. Most of the complexes have θ near 180° though some have smaller values, the lowest being 164° among the complexes investigated. Hence, we propose a small modification of Legon-Millen rule that is applicable for geometries of all the X-bonded complexes: *The equilibrium angular geometry of an X-bonded complex A•••X-D can be predicted by assuming that the bond axis of the X-D is collinear with the line connecting A and X, with A being an atom or a bond centre, electrons of which are the acceptors of X- bond from XD.* We expect this rule to be applicable when there is one dominant acceptor site in A. Legon and Millen's third rule suggests that a lone pair succeeds over a π pair when either of them could be the acceptor. Though, all the acceptors chosen in our study have only one dominant site, we note that the binding energy increases in the order $\sigma < \pi <$ unpaired < lone pair, broadly in agreement with the third rule. We further note that there can be unusual acceptors, such as CH_4[38] in which the acceptor site may be an electron rich region in the tetrahedron face center which cannot be thought of as a simple σ or π bonded pair of electrons. Even in this case, the O-H•••C is linear.

A closer inspection of Table 1 reveals some interesting observations. For D = OH, the *θ(A•••X-D)* = 180° for all A•••LiOH complexes. However, for A•••ClOH complexes, it is about 177° and for A•••HOH complexes it varies from 170-179. The difference appears to be due to possible secondary interactions for ClOH and H_2O, both of which are bent whereas LiOH is linear. The linear geometry of Li-OH donor moiety is because of the more ionic nature of Li-O bond while the corresponding bonds in H-OH and Cl-OH donor moieties have significant covalent nature. The atoms in molecule (AIM) theoretical analysis supports this observation (*vide infra*). In general, when θ is below 180°, it is suggestive of some long range secondary interactions. For example, θ for C_2H_4•••Li-D complexes vary from 164° for D = Br to 180° for D = H. Except for D = H, all other complexes are somewhat bent indicative of some attractive interaction between D and C_2H_4.

Structure: The A•••X distance

In the earlier days, for a hydrogen bonded complex D-H•••A, the distance between D and A was expected to be less than the sum of van der Waals radii of D and A.[4–7] It has now been well established that such conclusions may only be applicable to strong hydrogen bonds. The use of van der Waals radii to conclude about hydrogen bonding has not been recommended in the recent IUPAC definition.[23] In recent years, the H•••A distance in DH•••A has been interpreted as the sum of hydrogen bond radii for DH and A.[39–42] We focus on the A•••X distance in the X bonded complexes in this section.

We group all the complexes investigated in this work in to two cases. Case I has the complexes having same donors (DX) with varying acceptors and case II has the complexes having same acceptors (A) with varying donors. The distances between A and X, *d(A•••X)*, for X = H/Cl varied for both cases, when either A or D was varied. These are broadly consistent with the hydrogen bond radii[39-42] and chlorine bond radii[43] recommended for various DX and A. For X = Li, the *d(A•••X)* distances are almost constant for case II. These could be thought of as the sum of Lithium bond radii for LiD and A. As A has been kept constant and the A•••D distances do not vary much, it is clear that the lithium bond radii are very similar for all LiD. It should clearly be due to the fact that all LiD have ionic bonds and the radii of Li in these molecules would be close to the ionic radii of Li^+. Indeed the AIM calculations reported later confirm this. For case I complexes, A•••Li distances vary and it is clearly due to the variation in the A radii. Another important difference is noted between H/Cl bonded complexes and the Li bonded complexes. For the latter the Li atom is nearly equidistant from both A and D whereas for all the H/Cl bonded complexes investigated in this work D-X is shorter than X•••A. (Table 1).

Stabilization energy for D-X•••A complexes

The stabilization energies for all the X-bonded complexes have been given in Table 1. Not surprisingly, it is observed that interaction energy is almost constant for the case II complexes for X = Li. There have been several reports earlier pointing out that the lithium bond is stronger than hydrogen bond[16,20,44–49] and we observe the same trend. There have been relatively fewer studies comparing H-, Cl- and Li-bonded complexes. Our results indicate that Li-bond is stronger than Cl-bond as well. The larger dipole moment of LiD molecules in comparison to HD and ClD molecules is primarily responsible for this difference.

For case I complexes in general, the stabilization energies for all three types of bonding decrease in the order A = $NH_3 > H_2O > C_2H_4 > C_2H_2 > CH_3 > H_2$. As pointed out in the previous section, this reconfirms the strength of acceptors as, lone pair > π pair > unpaired electron > σ bonded pair. For case II when the A is kept fixed and DX varies, hydrogen and chlorine bonding show similar behaviour. The order for D is F > NC > Cl > Br > OH > CN > CCH for hydrogen bonding with some exceptions and F > NC > OH > CN > CCH for chlorine bonding without exceptions (Table 1). For the diatomic hydrogen halide donors, HF, HCl and HBr, the binding energy correlates well with the dipole moment of the donors, 1.82 D, 1.08 D and 0.82 D, respectively. However, dipole moment trends cannot explain the trends in stabilization energy for other DH. For example, the dipole moment of HCN and HNC are both close to 3.0 D but A•••HNC complexes are twice as stable as A•••HCN complexes. Interestingly, the binding energy correlated better with the charge on H atom in these cases. For example, the charge on H atom in HCN is 0.24 but that in HNC is 0.57. The A•••HCCH complexes are very close in stability to A•••HCN complexes. The charge on H atom in HCCH is 0.17 though the molecular dipole moment is zero (See supporting material Table S1). Clearly, the charge on H in DH is more important and at best one can think about bond dipoles for polyatomic donors. We note that the stabilization energies for Cl-bonded complexes follow similar trend.

As already mentioned, Li-bonding is more stable than H/Cl bonding for the same D and A. Moreover, we note that the stabilization energies of DLi•••A varies dramatically when A changes from H_2 (9.9 – 11.7 kJ mol^{-1}) to H_2O (76.7 – 95.0 kJ mol^{-1}). For the same A, the stabilization energy decreases in the order CN > NC > Br > Cl > CCH > H > F > OH. Note that CN tops the list here whereas for H/Cl bonding, it appeared towards the bottom of the list. This trend is in general similar to the trend observed in dipole moment of DLi. The values of dipole moments in Debye are Li-CN(9.5) > Li-NC(8.7) > Li-Br(7.4) > Li-Cl(7.3) > Li-CCH(6.2) > Li-H(5.9) > Li-F(6.5) > Li-OH(4.7). The available experimental dipole moments[50] are in reasonable agreement with the calculated dipole moments.

It is worth reemphasizing a comparison between hydrogen bonds and lithium bonds. For A•••LiD (D = F/Cl/Br) the trend for binding energy is A•••Li-Br > A•••Li-Cl > A•••Li-F and for A•••HD, there is a reverse trend i.e. A•••H-F > A•••H-Cl > A•••H-Br. However in both cases, the dipole moment follows the same trend. The HD molecules are covalent and the dipole moment increases with the electronegativity difference between H and D. The LiD molecules are all ionic and the charge on Li is nearly the same for all D and the dipole moment increases as the Li-D distance increases in the order LiBr>LiCl>LiF. However, we caution the reader that, description of these complexes as simple dipole-dipole interactions would be incomplete if not incorrect. Two dipoles can arrange in two ways: linear or anti-parallel and if the interaction is pure electrostatic, linear arrangement should be the global minimum.[27] Neither hydrogen bonded complexes such as HF dimer nor lithium bonded complexes such as LiF dimer have linear global minimum.[51]

Elongation in H-D bond length and red shift in H-D frequency on complex formation are well known characteristics of hydrogen bounded complexes, [1–7] though now there are some examples for blue-shifting hydrogen bonds.[23] However, for DCl•••A and DLi•••A complexes, the D-X stretching can get mixed with some other modes in A. Such mode mixing between vibrations in donor and acceptor can cause apparent red- and blue-shifting and so, for chlorine- and lithium bonded complexes, frequency shift is not a useful measure.[16] In the examples included in this investigation, most lithium bonded complexes show a small blue-shift and all hydrogen bonded complexes show red-shift. The chlorine bonded complexes show red- or blue-shifts (Table 1).

Atoms in Molecules (AIM) Theoretical Analysis

Bader's AIM theory has been successfully applied to study the properties of conventional and non-conventional Hydrogen bonds, halogen bonds and lithium bonds. The comparison between hydrogen and halogen bond has been done extensively.[16,19,52–54] Carroll and Bader[55,56] initially proposed several criteria based on electron density topology. Koch and Popelier[18] provided a good summary listing out eight criteria for C-H•••O hydrogen bonds. We begin our discussion by examining these criteria for all the H/Cl/Li bonded complexes investigated here. The sign of Laplacian is used to distinguish closed-shell and shared-shell interaction by Koch and Popelier[18] following the work by Bader.[56] This has been shown to be ambiguous and several other criteria have been proposed by Cremer and Kraka[57], Espinoza[58] and Amezaga et al.[19] These are also considered in our discussion.

Koch and Popelier Criteria

Topology

The presence of a bond critical point (BCP) and bond path between X and A is the first criterion and this is satisfied in all 100 complexes. For most of the cases, the bond paths are linear. Figure 1 shows the optimized structures and electron density critical points for six of the complexes all having an one-electron X-bond acceptor, DX•••CH_3 for D = F/OH and X = H/Cl/Li. Figure S1 given in supporting information features all 100 complexes.

Electron Density at the Bond Critical Point.

The values of electron density at all BCPs are relatively low in comparison to that for a covalent bond, which is to be expected. The reported range for C-H•••O hydrogen bond by Koch and Popelier[18]is 0.002-0.034 a.u. and it can be compared to results for Li-bond, 0.0142-0.0274 a.u.[20] and for Cl-bond, 0.02-0.06 a.u.[19]. These values do depend on the range of examples included in these studies and also to some extent the level of theory and basis sets used.[59] In the present study, the ranges are 0.0102-0.0642 a.u., 0.0098 - 0.0320 a.u. and 0.0042-0.0687 a.u. for H-bond, Li-bond and Cl-bond respectively. The upper limit in our study is larger compared to that recommended by Koch and Popelier as our work has considered a wide range of donors and acceptors. In general, NH_3 as acceptor leads to the upper limit quoted above. The NH_3•••Cl-F complex has the highest value of electron density at BCP, 0.0687 a.u. and it is comparable to earlier work[19].

It has been well established that there is a strong correlation between the electron density at BCP and the bond energy. As mentioned earlier, this work began with a main objective of verifying our earlier results on a few selected complexes.[16] Indeed, this work covering 100 complexes not only confirms the linear relationship but also the distinctly different slope for Li-bonded complexes in comparison to H-/Cl- bonded complexes.[16] The correlation coefficients are 0.97, 0.96 and 0.88 for lithium, chlorine and hydrogen bonding respectively and the corresponding slopes are 3271, 777 and 776. (Note that Reference 16 had the binding energy in kcal mol^{-1} and so the slopes were correspondingly smaller) The results are presented in Fig. 2 and Table S6 in supporting information. Our results are consistent with published reports on similar complexes[19,20] and a comprehensive summary is given in supporting information, Table S9.

The correlation coefficient for hydrogen bonded complexes mentioned above is relatively lower than that for Cl/Li bonded complexes. It may be noted that Koch and Popelier had concluded in their work that[18] "*linear correlation is excellent as long as the acceptor atom remains unchanged within the set.*".

As they already had the donor fixed as C-H, their results imply that the correlation will be good for similar donors and acceptors. Considering this, the correlation we have found for the range of donors and acceptors appear to be quite reasonable. In any case, several fits were tried for case I (donors constant) and case II (acceptors constant) complexes. The correlation coefficients and their corresponding slopes and intercepts for all sets (case I and II) are given in Table SM6. We note that the correlations are excellent for case I complexes for all three bonding. For case II, correlations are much better for Cl-bonding than Li-bonding and H-bonding. We note that in general keeping the donor fixed produces better correlation. Our conclusion is in agreement with the results of Li Bian[60] and "*proton donor is more important than proton acceptor in hydrogen bond formation.*"

Another interesting fact came out when we plotted binding energy vs electron density at BCPs for typical type of ionic and covalent bonds in DX along with the X•••A bonds. For this analysis, the donors were restricted to be diatomics i.e. D was F/Cl/Br only. The results are shown in Figure 3. Extrapolation of the plot for Li-bonding leads towards the ionic bond (D-Li) while H-/Cl-bond lead towards covalent bonds (D-H/D-Cl). This analogy was expected when the slopes in such a plot for ionic (LiD) and covalent (HD and ClD) molecules were determined. Hydrogen bonding has been thought of as a link between covalent bonding and van der Waals interactions for long. In particular electron density at the BCP has been used to describe 'hydrogen bonding without borders' by Parthasarathi et al. who investigated a range of 'hydrogen bonded complexes'.[61] Our comparison of H/Cl/Li-bonded complexes and the covalent/ionic molecules, clearly show that such 'bonding without borders' can be extended to all inter- and intra-molecular bonding. Clearly, one can think about a conservation of bond order, that includes covalency and ionicity, *vide infra*.

The Laplacian of the Charge Density at the Bond Critical Point

As mentioned earlier, the sign of the Laplacian of electron density at the BCP, $\nabla^2\rho$, has been used to differentiate shared-shell (covalent) and closed-shell (ionic, non-covalent, van der Waals etc…) interactions. If it is positive, there is electron accumulation in between the two atoms indicative of shared-shell, covalent, interaction. If it is negative, there is charge depletion between the two atoms indicative of closed-shell interactions. For typical hydrogen bonded systems, $\nabla^2\rho$ are positive. It is indeed positive for ionic and typical intermolecular bonds [62]. For example, previously reported ranges in $\nabla^2\rho$ for Li-bond[20], H-bond[18] and Cl-bond[19] are 0.06-0.21 a.u., 0.024-0.139a.u. and 0.04-0.14 a.u., respectively. The values of $\nabla^2\rho$ at BCP for Li-, H- and Cl-bonding are given in Table 2 and ranges for these bonding are 0.0527-0.2584 a.u., 0.0284-0.1050 a.u. and 0.0183-0.1422 a.u. respectively. For comparison, $\nabla^2\rho$ values at the BCP of X-D bonds are 0.676, -2.849 and -0.173 for Li-OH, H-OH and Cl-OH monomers respectively. Li-O bond in Li-OH molecule is ionic and $\nabla^2\rho$ has a large positive value whereas the Cl-O and H-O bond in ClOH and H_2O are covalent and $\nabla^2\rho$ have negative values. Indeed, this difference in the nature of bonding does affect the structure and Li-OH is a linear molecule while H_2O and ClOH are bent having a V-shape.

Cremer and Kraka[57] have showed that the characterization of bond on the basis of Laplacian of electron density can lead to erroneous conclusions. For instance, they have shown that the $\nabla^2\rho$ is positive for some strongly covalent double/triple bonds, as in CO. They suggested considering the potential, $V(r_c)$, kinetic, $G(r_c)$, and total, $H(r_c)$, electron energy densities at BCP. We denote these as V, G and H from now on. For shared-shell interaction, the potential energy dominates, $|V| > G$ and H is negative, whereas for closed-shell interaction the kinetic energy dominates, $|V| < G$ and H is positive. Another similar criterion was proposed by Espinoza[58] on the basis of the ratio $|V|/G$. For closed shell interaction, $|V|/G < 1$ and for shared shell interaction, $|V|/G > 2$. Interaction is taken as intermediate type if the ratio falls between these two limits. There is no sharp boundary between the two types of bond. Some strongly bound complexes have $|V|/G$ value greater than 1.00 and it is taken as evidence for partial covalent nature.

For the 100 examples chosen in our study, both these criteria were examined. Hydrogen bonded complexes fall in the closed-shell or intermediate region (See Figures 4 and 5 and Table 2). Chlorine bonded complexes fall mostly in the closed-shell interaction regions except for the three ClF complexes. All the lithium bonded complexes have closed-shell interaction irrespective of the criterion used. For lithium bonded complexes, the total energy H is positive in every case and $|V|/G$ ratios is close to and smaller than 1.00 (Table 2 and Figures 4 and 5). Clearly, hydrogen bonding and chlorine bonding are similar but lithium bonding has distinct characteristics. Correlations between binding energy, electron density at the BCP and mutual penetration also lead to the same conclusions (*vide infra*).

Sosa and co-workers have proposed another characteristic of shared-shell interaction as the ratio $|\lambda_1|/\lambda_3$, which is greater than 1[19] (see Table 2). Among the three eigen values of the Laplacian, λ_1, λ_2, and λ_3, the first two are in general negative and the third one positive as the electron density at BCP is maximum in the two directions orthogonal to the bond and it is a minimum along the bond path, leading to the (3,-1) bond critical points. Hence, when this ratio is more than one, the maximum (electron accumulation) is steeper than the minimum (electron depletion). In other words, this is the ratio of the perpendicular contraction to the parallel expansion along the bond path. They had considered only the hydrogen and halogen bonded complexes. We extend their approach for lithium-bonded complexes and also for the 'covalent' D-H/D-Cl and 'ionic' D-Li bonds in our work, see Figure 6. The results presented in Figure 6, in comparison with those from Figures 4 and 5, suggest that the $|\lambda_1|/\lambda_3$ ratio for closed-shell interaction is less than 0.25. All intra-molecular bonds in Li-D and the intermolecular bonds in DLi•••A considered in our work have $|\lambda_1|/\lambda_3$ less than 0.25. For lithium bond, these ratios are almost constant for case I and overall variation is very small (0.161-0.192). On the other hand, this ratio for hydrogen bonds goes up to 0.42 for BrH•••NH_3. Based on these results, we propose the following. The $|\lambda_1|/\lambda_3$ ratio is less than 0.25 for closed-shell interaction and greater than 1 for shared-shell interaction. The values in between 0.25-1.00 represent an intermediated region.

Based on all the topological parameters derived from the Laplacian of electron density at BCP, sign of $\nabla^2\rho$, the ratio $|V|/G$, sign of H and $|\lambda_1|/\lambda_3$ ratio, it is clear that the 'ionic bond' in Li-D and the lithium bond in DLi•••A are both clearly closed-shell interactions. Hydrogen bond and chlorine bond on the other hand can be in the intermediate region where some extent of covalency can play a role. A natural bond orbital analysis can give the extent of covalency in all these interactions and that will be discussed later.

Mutual Penetration

Mutual penetration was considered as the necessary and sufficient condition for hydrogen bond by Koch and Popelier[18]. It is the summation of the difference between the non-bonded radii and bonded radii of both acceptor A and the bonded atom X. Non-bonded radii is the distance from nucleus to the point where the electron density value is 0.001 a.u. in monomer but the distance should be measured in the direction of approach of the bonded partner [18]. For hydrogen/chlorine bonded complexes, the binding energy is strongly correlated to the mutual penetration. In lithium bonded complexes, there are two regions: penetration linearly depends on binding energy and penetration remains constant as binding energy increases (Fig. 7). Generally for strongly bound complexes (>63 kJ/mole) penetration remain constant e.g. for complexes H_2O/NH_3•••Li-D while in weakly bound complexes (<42 kJ/mole) it is linearly dependent (e.g. for complexes $CH_3/C_2H_4/H_2$•••Li-D, correlation coefficient is 0.96). For case II lithium bonded complexes, the bonded radii of both acceptor and Li-atom remain constant and penetration is therefore constant (See Table S10). Not surprisingly, the bonded radii of Li in the strongly bound complexes were very close to the ionic radii of Li^+, 0.73 Å. In the weaker complexes, such as H_2•••LiOH, the bonded radii of Li is 0.88 Å. As noted earlier, Li is equidistant between D and A in these strongly bound complexes. What is perhaps surprising is that LiD could form complexes with weak acceptors and these are not purely 'electrostatic'. For case 1 complexes, when the donor is kept fixed, the radii of both acceptor and lithium varied and showed linear relationship with a correlation coefficient 0.96 for all complexes (Table S7).

For the chlorine bonded complexes, both case 1 and 2, there is a strong correlation between the overall penetration and binding energy (Table S7). For hydrogen bonded complexes, there is a general correlation between penetration and binding energy. However, the correlation is better for case 1 than case 2 (Table S7). However, it is clear that the hydrogen and halogen bonds behave differently compared to the lithium bonds. Interestingly, the difference could well be due to the fact that the donors (DH/DCl) are 'covalently bonded' in the former case and 'ionic' in the later case (DLi). This in turn influences the nature of the DX•••A bond.

Since binding energy correlates well with electron density and also with mutual penetration, it is logical to think about the correlation between electron density and penetration (Fig. 7). Surprisingly, this is the best correlation we observed among the binding energy vs electron density, binding energy vs penetration and electron density vs penetration. To the best of our knowledge, electron density vs penetration correlation has not been analyzed before. This correlation assumes significance, given the fact that van der Waals radii are still used as the 'non-bonded radii' in analyzing crystal structures to make conclusion about penetration. For example, it was concluded that C-H•••O contacts are 'hydrogen bonds' and C-H•••π contacts are 'van der Waals interaction' using this arbitrary non-bonded radius to measure penetration.[63] However, both these interactions satisfied the other criteria of Koch and Popelier for 'hydrogen bonding'. The correlation between electron density and binding energy is useful for analyzing crystal structure and also intramolecular hydrogen bonds as there are no direct methods available for measuring the binding energy in these cases. In closing, we point out that the exclusion of C_2H_2•••H-D and NH_3•••Cl-D from H-bond and Cl-bond respectively, improves the correlation coefficient.

Net charge on bonded atoms

Net charge on atom is defined as the difference between nuclear charge and average number of electronic charge N(A) on the atom A (Table 2). Koch and Popelier had observed that there is a loss of the charge on the hydrogen atom on hydrogen bond formation. The same is observed for Li atom in the lithium bonded complexes. However, for chlorine atom, there is gain of charge on chlorine bond formation and it has been noted in earlier work as well.[19] We note that in all complexes and monomers (Li-D), Li atom has charge close to +1 (Table S1). In this criterion, H and Li behave similarly but Cl is different.

Energy of the bonded atoms

Generally H-atom is destabilized on hydrogen bond formation. However, both Li and Cl atoms get stabilized on X bond formation (See Table 2 and Table S2).

Dipolar Polarization

According to this criterion, there is a loss in dipole moment of the H atom involved in hydrogen bonding. This has been observed for most of the H- and Cl-bonded complexes in this investigation. However, for most of the Li-bonded complexes, there is gain in the dipole moment of Li-atom on complex formation (see Table 2 and Table S3). However, it is worth noting that the exceptions have values which are very close to zero.

Volume of the bonded atom

The last criterion is the change in atomic volume after complex formation. For C-H•••O, hydrogen bonds Koch and Popelier noted a decrease in atomic volume of H. It is observed in all hydrogen and chlorine bonded complexes in this work. However, for Li-bond, there is an increase in volume on complex formation. (See Table 6 and Table S4)

Overall, it is clear that, the eight criteria found by Koch and Popelier for C-H•••O hydrogen bonds cannot be simply extended to other intermolecular bonding. Hydrogen and chlorine bonds behave more similarly and lithium bonds are different. The old periodic tables having hydrogen on top of both the alkali and halogen groups are indeed sensible.

NBO analysis

Bond elongation and weakening of D-H bond on complexation are well known features of the hydrogen bond. This leads to the signature red-shift for a hydrogen bond, though we now know of blue-shifting hydrogen bonds as well.[16,23] Weakening and lengthening of the D-H bond is attributed to the new 'bond' formed by H with A. Just by comparing the O-H bond distance with the H•••O bond distance in O-H•••O hydrogen bonds, Pauling[7] had concluded that the O•••H hydrogen bond should have a covalency of 5-10 %. Though, this interpretation supported by the red-shift in D-H has been well documented and accepted, as mentioned in the introduction the term 'hydrogen bond' has been considered incorrect by some. Of course, chemical bonding has itself been a source of confusion for long.[64] What is surprising is that most of the discussions about the ambiguity of 'chemical bonding' completely ignore 'ionic bond'. In this work, comparing the complexes of the 'covalent' DH and DCl along with the 'ionic' DLi has given us an opportunity to look at the ionicity and covalency of not only the donor D-X bond but also the intermolecular X•••A bond. Could one expect that the covalent D-H and D-Cl will become weaker and the H•••A/Cl•••A bond will gain that much covalency? What about the ionic D-Li bond? It is only natural that the ionicity of D-Li bond is reduced and the Li•••A bond gains that much ionicity. Will it also gain covalency? The NBO analysis reveals the answers to all these questions.

Weinhold's Natural Bond Orbital[37] method allows one to calculate the covalency and ionicity of the bonds in addition to determining the commonly used second order perturbation energy due to the n-σ* overlap. The later is the cause for the weakening D-H bond and the associated red-shift. It is indeed this overlap that gives covalency to the H•••A bond and legitimized the 'hydrogen bond' nomenclature. In this work, we focus on calculating covalency and ionicity of both D-X and X•••N bonds for H_3N•••XD (D = F/Cl/Br, X= H/Li) and H_3N•••ClF complexes. There were four resonance structures considered by the NBO programme for these complexes and their weights are presented in Table 3 and Figure 8. The total ionicity of X-D bond in complex is calculated by summing the ionicity of resonance structure 1 and 2 while total covalency is the same as covalency of structure 2 since structure 1 is purely ionic. Structure 3 has the X•••N bond but no D-X bond, with the D acquiring one more lone pair. This structure is the most important in this work as this considers the X•••N bond. Structure 4 has a bond between D and N with the X acquiring the lone pair. Structure 4 contributes about 1.5-2.5 % for DH complexes but does not contribute for DLi complexes. Structure 1 does not contribute for D-H and D-Cl complexes. With these resonance structures, the ionicity and covalency of both the D-X and X•••N bonds were calculated. The results are shown in Table 3.

The results given in Table 3 reveal some obvious conclusions and some not so obvious. First, we mention the obvious one. The Li-D molecules are predominantly ionic, with the LiF being 100 % ionic and LiBr 99.84 % ionic. For the hydrogen halides, HF is more ionic (57.0) %) than HCl (27.5 %) and HBr (20.2 %), the rest being covalency. The ClF molecule is more covalent (62.2 %) than ionic. On complex formation, the DH molecules loose covalency. As a result, the D-H bond becomes more ionic and the H•••N bond is formed. The H•••N bond has significantly more ionic character but includes a small non-zero covalency. Interestingly, perhaps not surprisingly, the DLi molecules loose ionicity, making the D-Li bond little more covalent and also forming the Li•••N bond. The FCl•••NH_3 complex is different in that the Cl-F bond looses both covalency and ionicity on complex formation, resulting in a stronger Cl•••N bond. The X•••N bond in all these complexes are significantly ionic but all of them including Li•••N have a small non-zero covalency. Even with Li-F which is 100 % ionic according to this analysis, the lithium bond in FLi•••NH_3 has a small covalency! Moreover, the Li_F bond also gains marginal covalency on lithium bond formation. From the data given in Table 3, the hydrogen bond is about 5 % covalent, lithium bond is about 2 % covalent and the chlorine bond is about 21 % covalent. If one adds the covalency and ionicity in X•••N and D-X bonds, one can see that there is a conservation of bond order. For lithium bonds, structure 4 does not contribute and the sum of ionicity and covalency in these two bonds add up to a 100 %. For hydrogen and chlorine bonds other resonance structures contribute about 1.5-2.5 %.

Electron density at BCP: A relook

Following the NBO analysis discussed above, it seemed obvious that the electron density at the BCP of D-X should decrease on complex formation and it might lead to the observed electron density at X•••A bond. It was decided to look at the correlation between the change in electron density at D-X BCP and X•••A BCP. To the best of our knowledge, and to our surprise, there appears to be no report of such an analysis. The correlation plots for hydrogen, chlorine and lithium bonds are shown in Figure 9. The correlation coefficients are respectable at 0.84, 0.90 and 0.81, for H-, Cl- and Li-bonding, respectively.

The data given in Figure 9 also shows that H- and Cl-bonding have some similarity and Li-bonding is different. The slopes for these correlation plots are close to one for hydrogen (0.9) and chlorine (1.1) bonding. This suggests that the weakening D-X bond is directly related to the formation of X•••A bond. The slope for Li-bonding is significantly larger at 4.7, though the electron density at Li•••A BCP as well as the difference in electron density at Li-D bond are both significantly smaller than those observed for H-/Cl-bonding cases. This in a way confirms the results from the NBO analysis, which suggests that the Li•••N bond has a small covalent character at the cost of loss of ionicity of Li-D bond. There are some H- and Cl-bonded complexes which have the electron density differences at D-X bond as negative. This implies that the electron density at the D-X BCP is actually increasing following the X•••N bond formation.

Clearly, one can expect a good correlation between the electron density difference at D-X with the binding energy and penetration and these plots are shown in the supporting information (Figure S3). As noted earlier, for Li-bonded complexes, these plots also show a linear region for weakly bonded complexes (where CH_3, C_2H_4 and H_2 as acceptor) and a plateau for strongly bonded complexes (H_2O and NH_3 as acceptor). Our analysis has focused on only the D-X and X•••A bonds and clearly both these bonds would be influenced by the other bonds in cases where both the donor and acceptor are polyatomic molecules. This is clearly shown in the case of A•••XCN (X = H/Cl) complexes, which show an increase in electron density at the X-C BCP following A•••X bond formation. A detailed analysis must include all the bonds in donors and acceptors. However, the overall correlation visible in Figure 9 provides some justification for focusing on the X•••A and D-X bonds.

It is worth reemphasizing that, irrespective of X from a D-X molecule involved in intermolecular bonding, the formation of X•••A bond leads to a conservation of bond order, if one takes care of both ionic and covalent character of both D-X and X•••A bonds. Clearly, the debate about whether all these intermolecular interactions should be called 'bonding' appears unnecessary. As mentioned earlier, much of the debate about the suitability of the term 'bond' ignores ionic bonding.

Before concluding, we must point out that conservation of bond order has been in the literature for long starting from the work of Pauling,[7] particularly with respect to the hydrogen bonding.[65] Coulson had used resonance structures, as in Table 3, to point out the covalent contribution in hydrogen bonds.[66] Majerz and Olovsson have extended the bond order concept and have shown that the bond order for H is conserved along proton transfer coordinate.[67] Mohri had discussed 'bond valences' in hydrogen bond with the assumption that the sum of bond valences for D-H and H•••A bonds is 1.[68] Golubev, Limbach and co-workers have used such valence bond order model to describe hydrogen bond coupling constants and chemical shifts observed in the NMR spectrum.[69] However, all these models have assumed that the D-H bond is 100 % covalent initially and on the D-H•••A bond formation, the D-H and H•••A bond orders are conserved to 1. In a way it is surprising, as rarely a chemical bond between two atoms in a molecule is 100 % covalent or 100 % ionic, as revealed by the data on monomers given in Table 3.

Pauling had estimated hydrogen bond to be about 5 % covalent just by comparing the H•••O bond length with the O-H bond length, assuming the later to be 100 % covalent, in an O-H•••O hydrogen bond.[7] However, our estimate of 5 % for covalency in hydrogen bond considers only the H•••A bond, suggesting that the rest of it is ionic. This was possible due to the extensive comparison of hydrogen and lithium bonding in this work. While the absolute estimates given for ionicity and covalency for D-X (in the monomer and complex) and X•••A bond could vary with the model and basis set, it is clear that assuming the D-X bond to be 100 % covalent is too simplistic. It is hoped that looking at the ionicity and covalency of D-X and X•••A bonds will bring chemistry back into the discussion on intermolecular interactions or should we say intermolecular bonding.

Conclusion

One hundred complexes formed between an acceptor A and donor DX, A•••X-D, have been theoretically investigated with X=H, Cl and Li at MP2(full)/aug-cc-PVTZ level. The unifying theme in all these one hundred complexes is that the angle D-X•••A is nearly linear for all X and A. If the X-bond acceptor has a well defined region of electron density such as one lone pair (NH_3), unpaired electron (CH_3), π electrons (C_2H_4/C_2H_2), σ electrons (H_2), the D-X approaches through this specific direction and it is enough to locate the other atoms in A. In all these specific cases, D-X approach A through the symmetry axis in A. If A has more than one region of electron density, as in H_2O having two non-degenerate lone pairs, the D-X•••O angle is linear, but that does not help in locating the H_2O plane. For hydrogen/chlorine bonded complexes, the binding energy has a strong correlation with the charge on H/Cl in DH/DCl, whereas for the lithium bonded complexes, there is a strong correlation with the dipole moment of DLi. In terms of the acceptors the binding energy increases as lone pairs > π-electron > unpaired electron > σ-electron. Lithium bonds are stronger than H-bond and Cl-bond.

We can summarize our results from the comprehensive AIM and NBO studies as follows.

1. There is a strong correlation between the electron density at the X•••A BCP and binding energy. The slopes of such correlation plots are similar for H-/Cl- bonding but distinctly different for Li- bonding. Extrapolation of these fitted lines leads towards ionic bond for Li-bonding and covalent bond for H-bonding and Cl-bonding. Moreover, there is a strong correlation between the electron density at X•••A BCP and mutual penetration. This could be very useful in determining the non-bonded radii in crystal structures instead of using 'van der Waals' radii, which can lead to ambiguous conclusions.
2. Comparing the values of $\Delta^2\rho$, H, |V|/G and $|\lambda_1|/\lambda_3$ ratio to differentiate closed-shell and shared-shell interactions leads us to suggest that $|\lambda_1|/\lambda_3 < 0.25$ be used as a limit for closed-shell interaction. For shared-shell interaction (i.e. a covalent bond), this ratio is 1.00 or more and the values between 0.25 – 1 could be considered as intermediate region.
3. Considering the ionicity and covalency of the D-X and X•••A bonds, it is clear that there is a conservation of bond order. When the ionicity and covalency are considered, it is also clear that the debate about whether 'hydrogen bond' is a misnomer is the result of a rather limited view of the term 'bond'.
4. Comparing the H-bond, with Li- and Cl-bonds have clearly shown that the difference in the nature of X•••A bonds for these three cases are significantly influenced by the nature of D-X bond. In any case, the X•••A bond has ionic (electrostatic) and covalent contributions for all X.
5. The conclusions reached here should be applicable for every atom in the periodic table, when it is involved in intermolecular bonding with another atom/bond centre.

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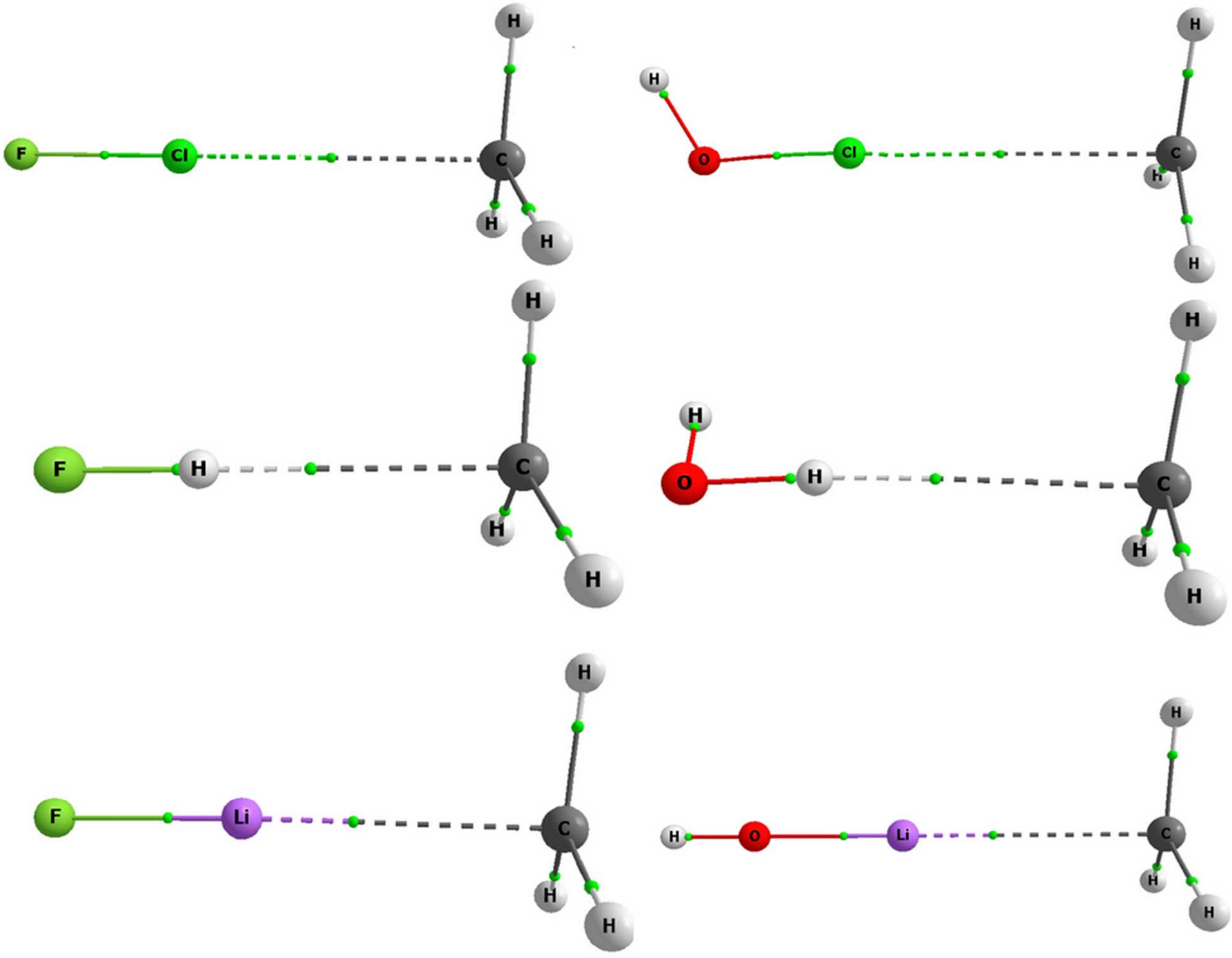


Figure 1. Structure of FX/HOX•••CH_3 (X = Li/H/Cl) complexes along with the bond critical points (green dots) and bond paths. Dotted lines denote inter-molecular bonds and solid lines denote intra-molecular bonds.

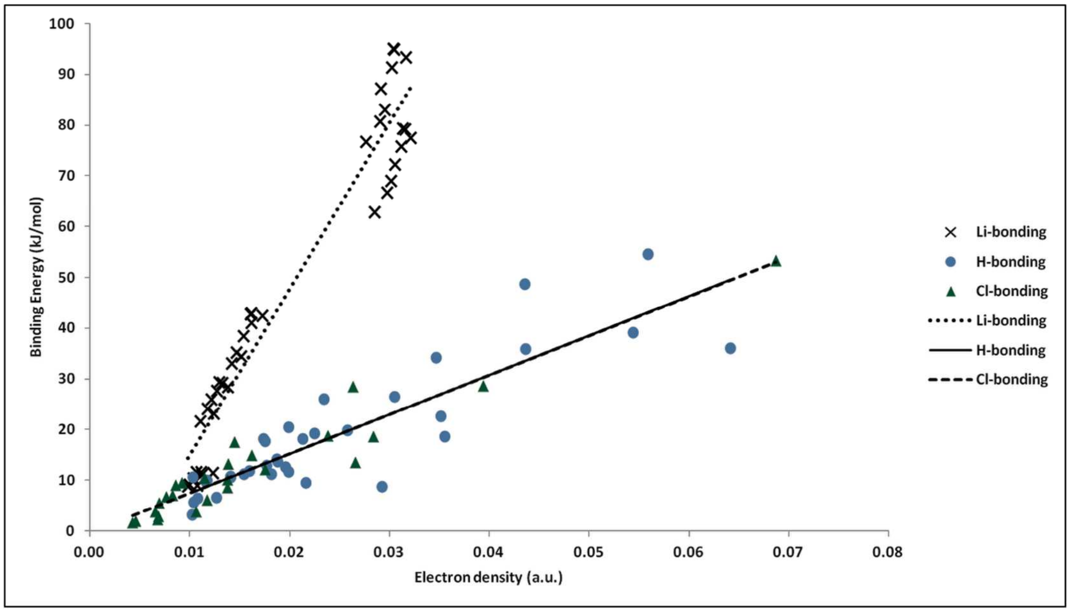


Figure 2. Correlation plots for binding energy and electron density for H-/Cl- and Li-bonding. Lines show the best linear fit.

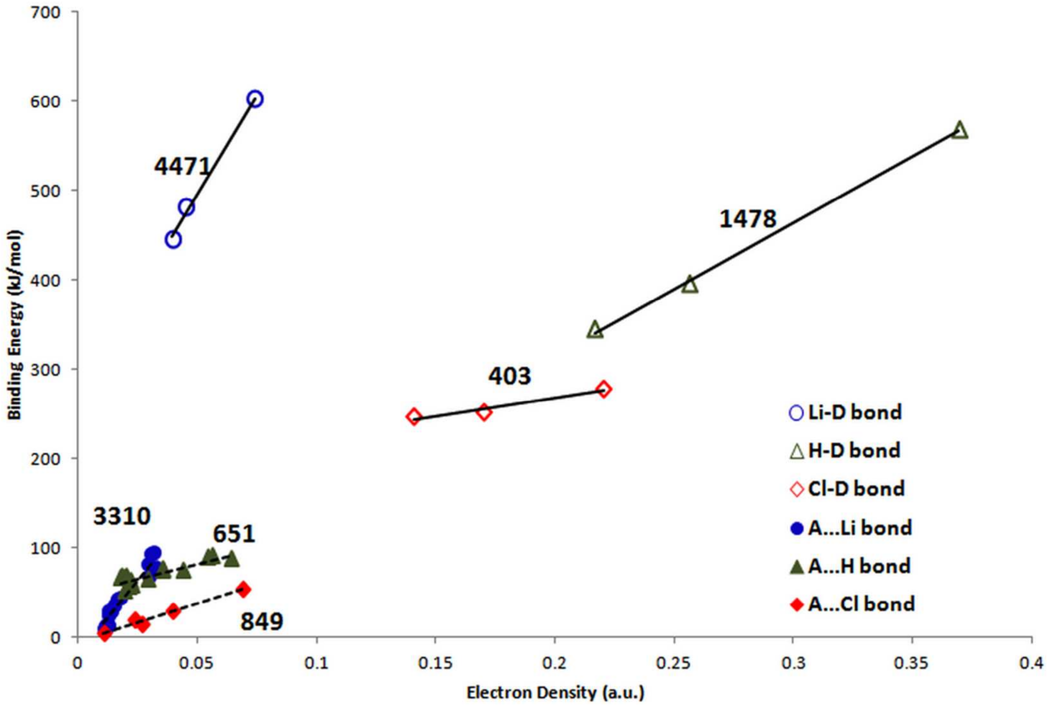


Figure 3. Comparison of electron density vs binding energy plots for H-, Cl-and Li-bonding with typical intramolecular bonds. **Slope of the best fit lines are shown.**

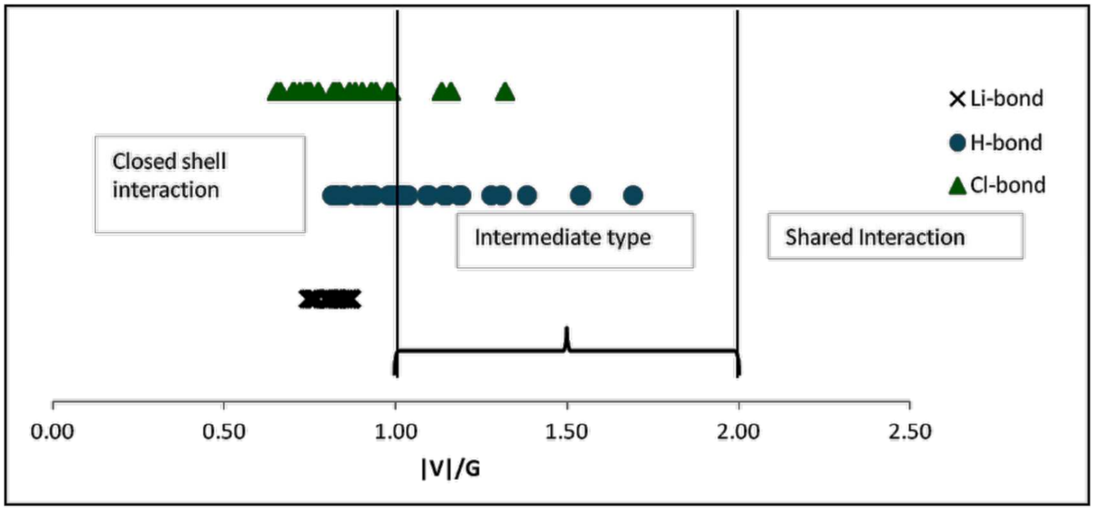


Figure 4. Plot of |V|/G ratio. |V(r)|/G(r) ratio for the characterization of bonding in three regions namely closed shell interaction, 5 intermediate and shared shell interaction.

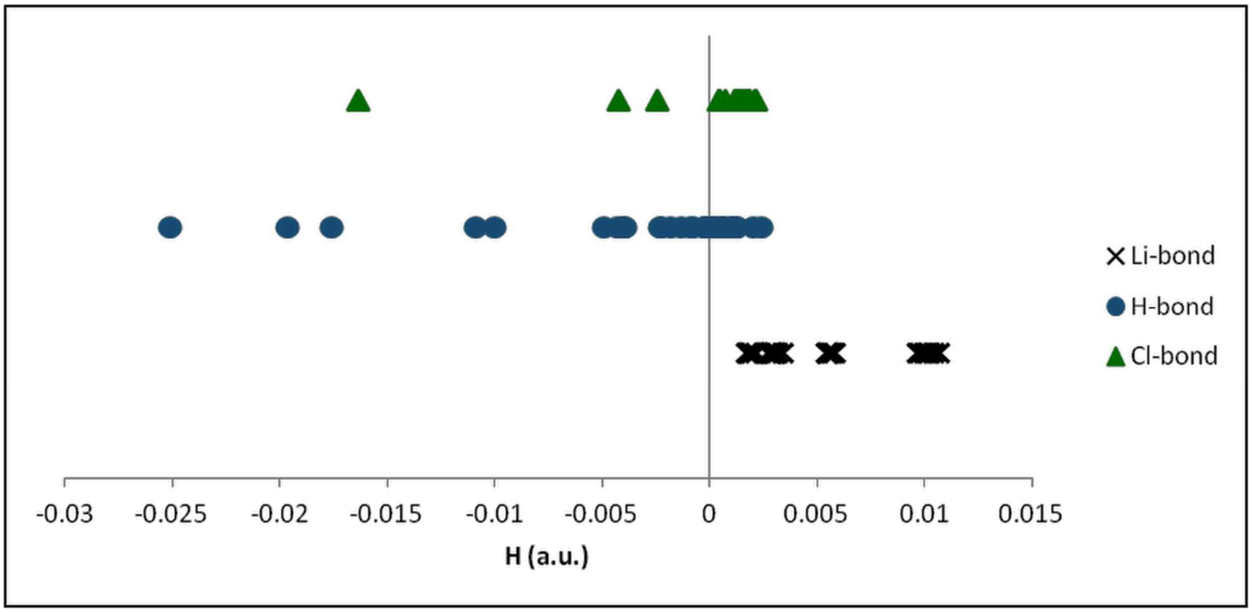


Figure 5. Plot of total energy density at BCP, H in atomic units, for H-, Cl- and Li-bonds (See Figure S2 for data on ionic and covalent bonds).

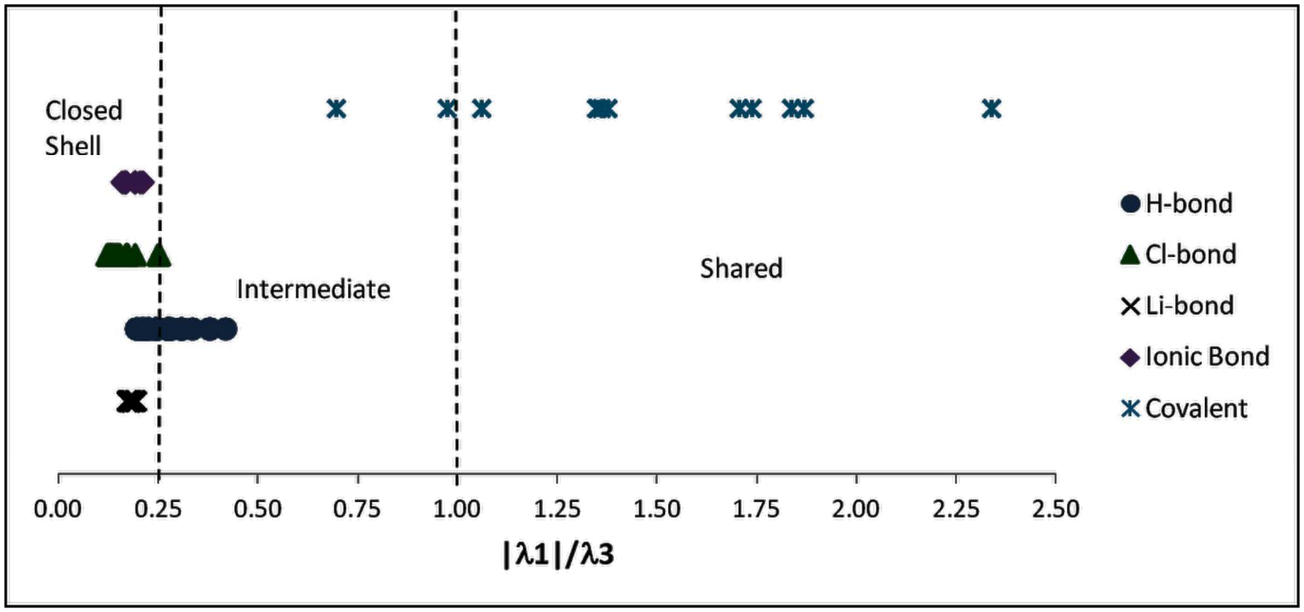


Figure 6. Plot of $|\lambda 1|/\lambda 3$ for various bonds having interactions classified as closed-shell, shared-shell and intermediate

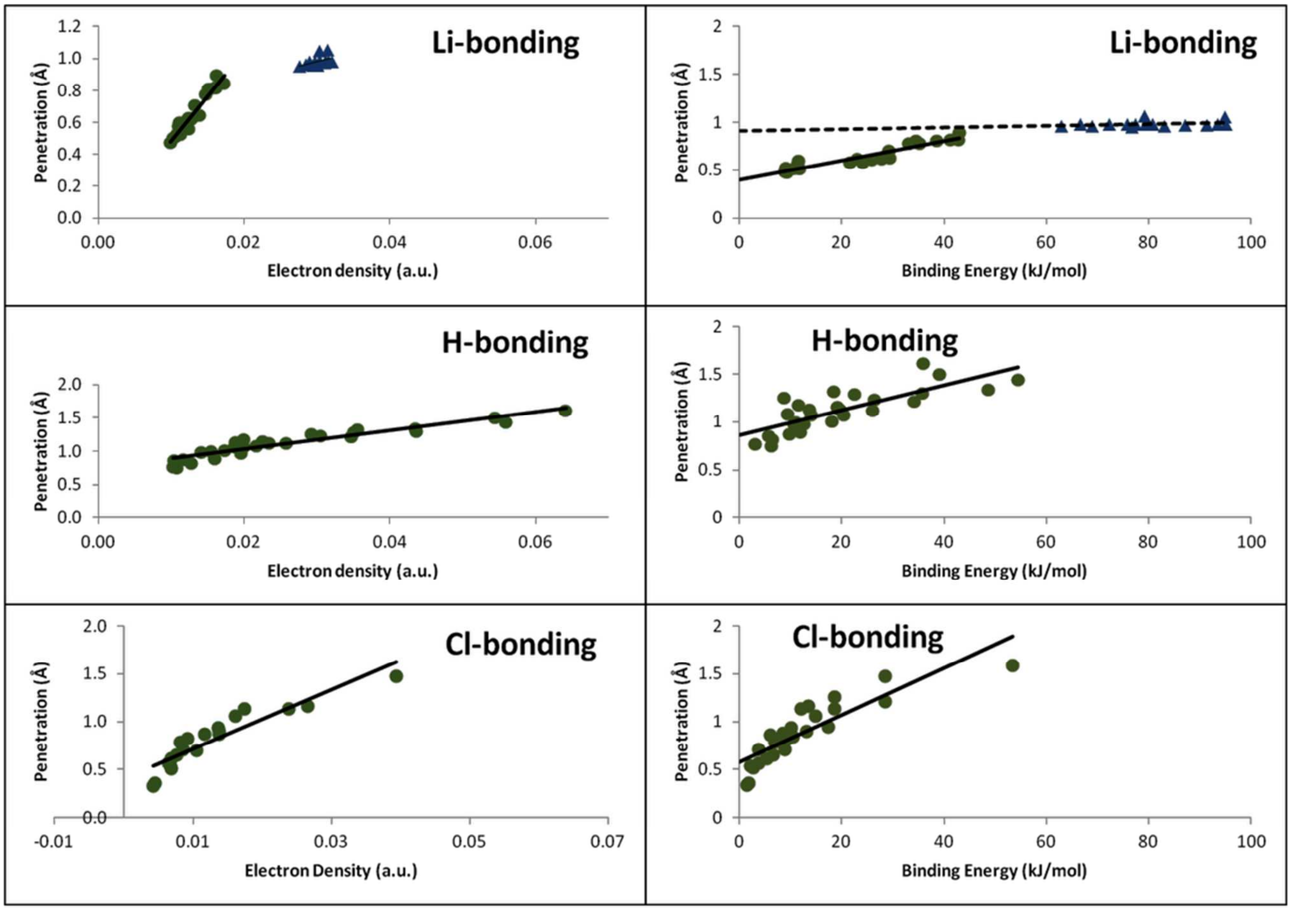


Figure 7. Correlation plots for penetration with electron density and binding energy.

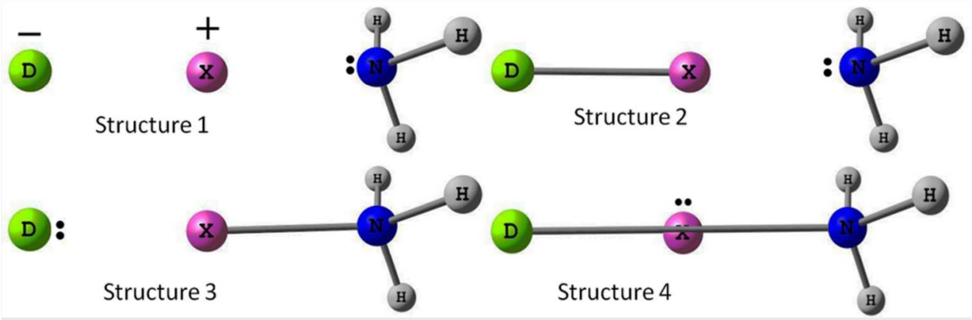


Figure 8. Various resonance structures of H_3N•••X-D complexes. A pair of dots represents a lone pair.

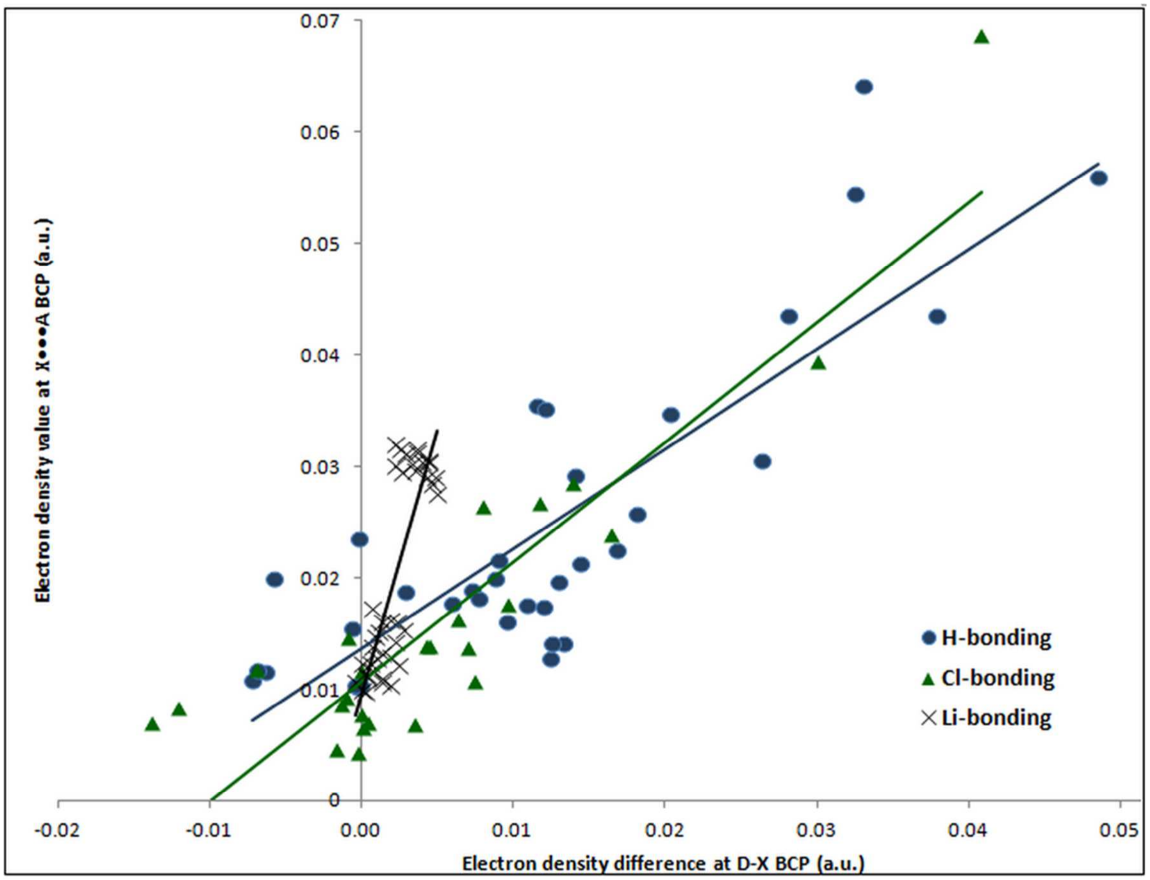


Figure 9. Correlation between difference in electron density at BCP of X-D with electron density at X•••A BCP.

Table 1. Important structural, spectroscopic and energetic properties of the X-bonded complexes. All the distances are in Å , angles are in degree and energies in kJ/mol.*

Complexes	d(A•••X)	d(X-D)	θ(A•••X-D)#	Frequency shift	Bond Elongation	Energy (BSSE)	Δ r_A + Δ r_X
				Lithium Bond			
CH_3•••LiCN	2.36	1.92	179.6	38	0.01	29.37	0.63
CH_3•••LiNC	2.35	1.78	179.8	-4	0.01	29.16	0.63
CH_3•••LiBr	2.32	2.18	179.9	-30	0.01	28.49	0.65
CH_3•••LiCl	2.36	2.04	179	-20	0.01	27.74	0.62
CH_3•••LiCCH	2.38	1.9	179.9	-20	0.01	25.94	0.61
CH_3•••LiH	2.39	1.59	177.9	30	0.01	24.06	0.58
CH_3•••LiF	2.37	1.59	178.3	1	0.01	23.14	0.62
CH_3•••LiOH	2.41	1.59	180	5	0.01	21.67	0.58
H_2O•••LiCN	1.89	1.93	180	-22	0.02	79.41	0.98
H_2O •••LiNC	1.89	1.79	180	-53	0.03	79.16	0.99
H_2O •••LiBr	1.88	2.19	180	-107	0.03	77.45	0.98
H_2O •••LiCl	1.89	2.05	172.4 (170)	-76	0.03	75.77	0.98
H_2O •••LiCCH	1.9	1.92	180	-66	0.03	72.26	0.98
H_2O •••LiH	1.9	1.61	180	63	0.02	68.99	0.96
H_2O •••LiF	1.91	1.6	180	-19	0.02	66.73	0.98
H_2O •••LiOH	1.92	1.61	180	3	0.02	62.89	0.96
NH_3•••LiCN	2.02	1.94	180	-17	0.03	95.02	0.98
NH_3•••LiNC	2.02	1.8	179.8	-31	0.03	94.89	0.98
NH_3•••LiBr	2	2.2	179.3	-99	0.03	93.43	0.98
NH_3•••LiCl	2.02	2.06	176.5	-63	0.03	91.42	0.97
NH_3•••LiCCH	2.04	1.92	180	-55	0.03	87.15	0.97
NH_3•••LiH	2.03	1.62	179.9	42	0.03	83.05	0.96
NH_3•••LiF	2.03	1.61	179.8	-7	0.02	80.71	0.98
NH_3•••LiOH	2.05	1.61	180	11	0.03	76.69	0.95
H_2•••LiCN	2.06	1.91	173.3	31	0	11.72	0.51
H_2•••LiNC	2.04	1.77	172.4	-19	0	11.59	0.53
H_2•••LiBr	2	2.17	179.8	-49	0	11.38	0.56
H_2•••LiCl	2.03	2.03	176.8	-25	0	11.17	0.53
H_2•••LiCCH	2.07	1.89	170.2	-25	0.01	10.46	0.51
H_2•••LiH	2.08	1.59	179.8	5	0	9.20	0.48
H_2•••LiF	2.06	1.58	179.2	-10	0	9.04	0.52
H_2•••LiOH	2.08	1.59	180	-7	0	8.91	0.49
C_2H_4•••LiCN	2.32	1.92	168.2	33	0.01	42.84	0.82
C_2H_4•••LiNC	2.31	1.78	171.6	-6	0.01	42.97	0.83
C_2H_4•••LiBr	2.28	2.18	163.9	-51	0.01	42.43	0.84
C_2H_4•••LiCl	2.31	2.04	174	-31	0.01	41.17	0.82
C_2H_4•••LiCCH	2.33	1.9	165.8	-26	0.01	38.53	0.81
C_2H_4•••LiH	2.35	1.6	180	40	0.01	35.19	0.78
C_2H_4•••LiF	2.34	1.59	178.5	0	0.01	34.43	0.81
C_2H_4•••LiOH	2.36	1.6	180	11	0.01	33.10	0.78
				Hydrogen Bond			
CH_3•••HBr	2	1.42	180	250	0.02	8.70	1.25
CH_3•••HCl	2.12	1.28	179.9	107	0.01	9.54	1.08
CH_3•••HF	2.12	0.93	179.9	117	0.01	12.55	0.98
CH_3•••HNC	2.23	1	180	169	0.01	11.84	0.89
CH_3•••HCN	2.44	1.06	179.9	1	0	6.32	0.75
CH_3•••HOH	2.34	0.96	174.3	46	0	3.14	0.82
CH_3•••HCCH	2.47	1.06	180	5	0	6.53	0.77
H_2O •••HBr	1.82	1.42	179.8 (133)	195	0.02	18.54	1.32
H_2O •••HCl	1.81	1.29	178.7 (133)	171	0.02	22.55	1.29
H_2O •••HF	1.69	0.94	178 (132)	329	0.02	35.77	1.3
H_2O•••HNC	1.79	1.01	179.3 (147)	346	0.02	34.14	1.22
H_2O •••HCN	2.02	1.06	179.7 (180)	52	0	20.42	1.07
H_2O •••HOH	1.93	0.97	172.4 (118)	106	0.01	19.79	1.13
H_2O •••HCCH	2.13	1.06	180 (180)	4	0	11.09	1
NH_3•••HBr	1.66	1.47	180	808	0.07	35.94	1.61
NH_3•••HCl	1.72	1.32	180	640	0.05	39.08	1.5
NH_3•••HF	1.68	0.95	179.9	703	0.04	54.43	1.44
NH_3•••HNC	1.8	1.03	180	673	0.04	48.66	1.34
NH_3•••HCN	2.09	1.07	180	182	0.01	25.98	1.12
NH_3•••HOH	1.95	0.97	171.1	238	0.01	26.48	1.23
NH_3•••HCCH	2.19	1.06	180	53	0.01	14.02	1.07

C_2H_4•••HBr	2.21	1.41	179.5	88	0.01	11.67	1.18
C_2H_4•••HCl	2.23	1.28	180	62	0.01	13.68	1.13
C_2H_4•••HF	2.09	0.93	179.5	169	0.01	19.20	1.16
C_2H_4•••HNC	2.24	1	179.3	212	0.01	18.07	1.01
C_2H_4•••HCN	2.46	1.06	179.4	23	0	9.79	0.87
C_2H_4•••HOH	2.33	0.96	169.8	52	0	10.63	0.98
C_2H_4•••HCCH	2.51	1.06	178.1	163	0	5.69	0.86
C_2H_2•••HBr	2.25	1.41	179.5	53	0.01	11.13	1.04
C_2H_2•••HCl	2.24	1.28	179.6	28	0.01	12.89	1.01
C_2H_2•••HF	2.11	0.93	179.4	124	0.01	18.16	1.04
C_2H_2•••HNC	2.22	1	179.2	183	0.01	17.66	0.95
C_2H_2•••HCN	2.44	1.06	179.2	10	0	9.87	0.81
C_2H_2•••HOH	2.32	0.96	178.9	36	0	10.59	0.89
C_2H_2•••HCCH	2.5	1.06	179.5	7	0	10.59	0.79
Chlorine Bond							
CH_3•••ClF	2.62	1.64	180	-123	0.02	13.51	1.16
CH_3•••ClCN	3.24	1.63	179.9	-32	0	5.40	0.61
CH_3•••ClNC	2.93	1.63	180	27	0.01	8.58	0.87
CH_3•••ClCCH	3.3	1.63	179.9	3	0	3.72	0.56
CH_3•••ClOH	2.97	1.7	176.7	-35	0.01	6.11	0.86
NH_3•••ClF	2.21	1.71	180	201	0.09	53.35	1.58
NH_3•••ClCN	2.93	1.63	180	-20	0	17.45	0.94
NH_3•••ClNC	2.61	1.64	180	67	0.02	28.45	1.21
NH_3•••ClCCH	3.04	1.64	180	10	0	10.42	0.84
NH_3•••ClOH	2.61	1.72	177.1	65	0.03	18.62	1.25
C_2H_2•••ClF	2.69	1.66	179.9	91	0.03	18.66	1.13
C_2H_2•••ClCN	3.2	1.63	179.3	-27	0	9.00	0.7
C_2H_2•••ClNC	2.96	1.63	179.8	25	0.01	13.22	0.89
C_2H_2•••ClCCH	3.26	1.63	179.1	5	0	6.61	0.65
C_2H_2•••ClOH	2.96	1.7	177.9	30	0.02	10.13	0.93
C_2H_4•••ClF	2.46	1.69	180	182	0.06	28.58	1.47
C_2H_4•••ClCN	3.19	1.63	179.9	-24	0	9.46	0.82
C_2H_4•••ClNC	2.9	1.63	180	40	0.01	14.90	1.05
C_2H_4•••ClCCH	3.24	1.63	179.9	7	0	7.03	0.78
C_2H_4•••ClOH	2.86	1.71	177.2	48	0.02	12.09	1.13
H_2•••ClF	2.66	1.64	179.8	28	0.01	3.77	0.7
H_2•••ClCN	3.08	1.63	179.6	-32	0	1.88	0.35
H_2•••ClNC	2.87	1.62	180	3	0	2.80	0.51
H_2•••ClCCH	3.12	1.63	179	1	0	1.55	0.33
H_2•••ClOH	2.89	1.69	177.3	6	0.01	2.26	0.53

[*] All the calculations have been done at MP2(full)/aug-cc-PVTZ level of theory. *d(A•••X)* is the distance between acceptor atom A and donor atom X, *d(X-D)* is the distance between X and D atoms and *θ(A•••X-D)* is the angle formed among denoted atoms. Bond elongation is the increment in bond length of donor moiety X-D after complex formation. Δr_A is the difference between bonded and non-bonded radii of acceptor A and Δr_X can be defined in same way for bonded atom X. Sum of these both quantity indicates mutual penetration for a particular complex. See text for more details.

[#] In the case of H_2O•••HD/H_2O•••LiCl complexes, the angle in parenthesis denotes the angle between the C_{2v} axis of H_2O and the D-X axis.

Table 2. Electron density topological and integrated atomic properties from atoms in molecules calculations.*

Complexes	ρ	$\nabla^2\rho$	H	|V|/G	λ1/λ3	diff. N(X)	diff. K(X)	diff. Mu (X)	diff. Vol(X)
				Lithium bond					
CH_3•••LiCN	0.0129	0.0604	0.002	0.87	0.181	-0.0306	-0.0032	0.0079	4.376
CH_3•••LiNC	0.0132	0.0617	0.002	0.87	0.181	-0.0218	-0.0193	0.0121	3.3
CH_3•••LiBr	0.0138	0.066	0.002	0.87	0.18	-0.0271	-0.0131	0.0041	5.1886
CH_3•••LiCl	0.0127	0.0629	0.002	0.84	0.177	-0.0189	-0.0174	0.0101	3.2089
CH_3•••LiCCH	0.0122	0.0578	0.002	0.85	0.179	-0.0252	-0.0039	0.0117	4.8335
CH_3•••LiH	0.0117	0.0567	0.002	0.84	0.177	-0.0188	-0.0173	0.0018	5.6099
CH_3•••LiF	0.0123	0.057	0.002	0.87	0.181	-0.0308	-0.0197	0.0114	4.7766
CH_3•••LiOH	0.011	0.0527	0.002	0.84	0.174	-0.0276	-0.0086	0.01	5.3635
H_2O •••LiCN	0.0313	0.2479	0.01	0.8	0.173	-0.025	-0.0136	-0.0015	1.8142
H_2O •••LiNC	0.0315	0.2493	0.01	0.81	0.173	-0.0202	-0.0304	0.0004	0.6
H_2O •••LiBr	0.032	0.2584	0.011	0.8	0.172	-0.0231	-0.0215	0.0019	1.8171
H_2O •••LiCl	0.0311	0.2496	0.01	0.8	0.172	-0.0235	-0.0226	0	1.6388
H_2O•••LiCCH	0.0305	0.2413	0.01	0.8	0.173	-0.0236	-0.014	0.0003	2.089
H_2O•••LiH	0.0301	0.2408	0.01	0.8	0.172	-0.0167	-0.023	0.0086	2.106
H_2O•••LiF	0.0297	0.2346	0.01	0.8	0.171	-0.0287	-0.0304	-0.0009	1.9613
H_2O•••LiOH	0.0285	0.2253	0.01	0.79	0.17	-0.0239	-0.0187	-0.0028	1.9147
NH_3•••LiCN	0.0304	0.185	0.006	0.87	0.182	-0.0334	-0.0236	0.0008	2.8981
NH_3•••LiNC	0.0304	0.1849	0.005	0.87	0.182	-0.0278	-0.0398	0.0043	1.7
NH_3•••LiBr	0.0316	0.1959	0.006	0.87	0.181	-0.0307	-0.0288	-0.0019	2.7546
NH_3•••LiCl	0.0302	0.1863	0.006	0.86	0.181	-0.0312	-0.0325	0.0029	2.6651
NH_3•••LiCCH	0.0291	0.1762	0.005	0.86	0.182	-0.0305	-0.022	0.0041	3.0564
NH_3•••LiH	0.0295	0.1814	0.006	0.86	0.182	-0.0253	-0.0314	0.004	2.9687
NH_3•••LiF	0.029	0.1767	0.005	0.86	0.181	-0.0369	-0.0399	0.0033	2.9674
NH_3•••LiOH	0.0276	0.1686	0.005	0.85	0.179	-0.0311	-0.0283	0.001	2.9832
H_2•••LiCN	0.0106	0.0611	0.003	0.75	0.181	-0.0166	0.0052	0.0025	2.5947
H_2•••LiNC	0.0111	0.0632	0.003	0.76	0.182	-0.0124	-0.0112	0.0007	1.7
H_2•••LiBr	0.0123	0.0716	0.003	0.77	0.181	-0.0186	-0.0048	-0.0008	3.2271
H_2•••LiCl	0.0112	0.0649	0.003	0.76	0.18	-0.0179	-0.0043	0.0062	2.9657
H_2•••LiCCH	0.0103	0.0599	0.003	0.75	0.179	-0.0164	0.003	0.0067	2.9434
H_2•••LiH	0.0099	0.0582	0.003	0.74	0.178	-0.0101	-0.0191	0.0012	3.0538
H_2•••LiF	0.0107	0.0599	0.003	0.77	0.182	-0.0227	-0.012	0.0067	3.1215
H_2•••LiOH	0.0098	0.0568	0.003	0.75	0.176	-0.0205	-0.0031	0.0057	3.63
C_2H_4•••LiCN	0.016	0.0765	0.003	0.83	0.192	-0.0306	-0.0092	0.0071	3.9658
C_2H_4•••LiNC	0.0162	0.0768	0.003	0.83	0.192	-0.0263	-0.0262	0.0112	3.2
C_2H_4•••LiBr	0.0172	0.084	0.003	0.83	0.191	-0.0314	-0.0203	0.0026	3.6092
C_2H_4•••LiCl	0.0161	0.0778	0.003	0.82	0.19	-0.031	-0.0204	0.0099	4.4998
C_2H_4•••LiCCH	0.0153	0.0742	0.003	0.82	0.19	-0.0292	-0.0094	0.0106	3.9949
C_2H_4•••LiH	0.0147	0.0708	0.003	0.81	0.191	-0.0209	-0.0186	-0.0006	4.9754
C_2H_4•••LiF	0.0151	0.0715	0.003	0.82	0.191	-0.0348	-0.0266	0.0101	4.7669
C_2H_4•••LiOH	0.0142	0.069	0.003	0.81	0.186	-0.0314	-0.0149	0.0083	5.1421
				Hydrogen Bond					
CH_3•••HBr	0.0292	0.0448	-0.005	1.31	0.306	0.0749	0.0204	-0.0018	-10.4812
CH_3•••HCl	0.0216	0.0406	-0.002	1.19	0.273	0.0164	0.0135	-0.0164	-5.5505
CH_3•••HF	0.0196	0.0386	-0.002	1.19	0.275	-0.0146	-0.0002	0.0003	-2.536
CH_3•••HNC	0.016	0.0362	-0.001	1.09	0.248	-0.0006	0.0071	-0.0032	-2.0575
CH_3•••HCN	0.0108	0.0285	0	0.93	0.211	-0.0045	-0.0135	-0.0001	-1.3104
CH_3•••HOH	0.0127	0.0326	0	1	0.227	-0.0267	-0.016	0.006	0.2321
CH_3•••HCCH	0.0102	0.0284	0.001	0.91	0.201	0.0123	0.0057	-0.0065	-1.2977
H_2O•••HBr	0.0355	0.0957	-0.004	1.15	0.276	0.1506	0.0457	-0.0318	-15.414
H_2O•••HCl	0.0351	0.0957	-0.004	1.14	0.276	0.0898	0.0413	-0.0531	-12.266
H_2O•••HF	0.0436	0.105	-0.01	1.28	0.309	0.019	0.0169	-0.0336	-6.9077
H_2O•••HNC	0.0347	0.1005	-0.004	1.15	0.276	0.0533	0.0324	-0.039	-8.7197
H_2O•••HCN	0.0199	0.079	0.002	0.89	0.21	0.0481	0.0054	-0.0249	-8.0512
H_2O•••HOH	0.0258	0.0843	-0.001	1.03	0.242	0.0135	0.0024	-0.0269	-5.8077
H_2O•••HCCH	0.0154	0.0642	0.002	0.82	0.193	0.0572	0.0213	-0.0275	-6.7261
NH_3•••HBr	0.0642	0.045	-0.025	1.69	0.419	0.2416	0.098	-0.0387	-21.9108
NH_3•••HCl	0.0544	0.0598	-0.018	1.54	0.379	0.1269	0.0705	-0.0635	-15.509

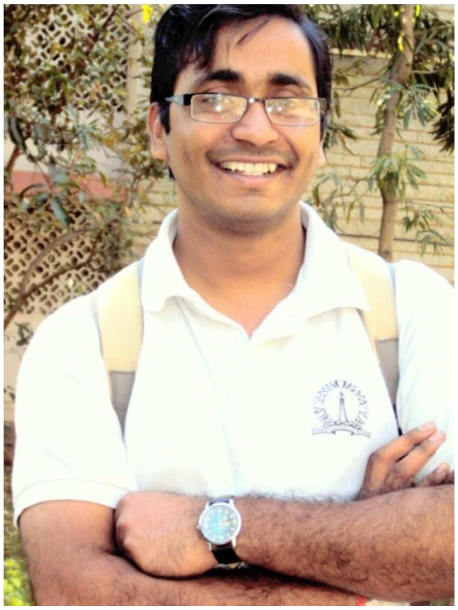
NH_3•••HF	0.0559	0.0681	-0.02	1.54	0.376	0.0047	0.0151	-0.0323	-6.7316
NH_3•••HNC	0.0436	0.071	-0.011	1.38	0.335	0.0529	0.0412	-0.04	-9.2083
NH_3•••HCN	0.0235	0.0649	0	1.01	0.242	0.0658	0.0197	-0.018	-9.0569
NH_3•••HOH	0.0305	0.0702	-0.004	1.18	0.282	0.0148	0.0098	-0.0261	-6.1991
NH_3•••HCCH	0.0187	0.0573	0.001	0.92	0.22	0.0745	0.0336	-0.0221	-7.7286
C_2H_4•••HBr	0.0199	0.044	0	1.02	0.275	0.0794	0.02	-0.0019	-9.4839
C_2H_4•••HCl	0.0188	0.0419	0	1.02	0.273	0.0289	0.0185	-0.0195	-6.5606
C_2H_4•••HF	0.0225	0.0454	-0.002	1.14	0.304	-0.0103	0.004	-0.0049	-4.112
C_2H_4•••HNC	0.0174	0.0408	0	1.01	0.269	0.0082	0.0136	-0.0078	-3.8803
C_2H_4•••HCN	0.0116	0.0317	0.001	0.85	0.225	0.0061	-0.0084	-0.0032	-2.4955
C_2H_4•••HOH	0.0141	0.0373	0.001	0.93	0.244	-0.019	-0.0111	0.0006	-1.7873
C_2H_4•••HCCH	0.0104	0.0298	0.001	0.82	0.213	0.0216	0.0101	-0.0091	-2.1387
C_2H_2•••HBr	0.0182	0.0465	0	0.98	0.241	0.0747	0.0166	-0.0052	-8.3424
C_2H_2•••HCl	0.0177	0.0454	0	0.98	0.243	0.0295	0.0171	-0.0224	-6.1983
C_2H_2•••HF	0.0213	0.0502	-0.001	1.1	0.272	-0.0054	0.0052	-0.0081	-4.2091
C_2H_2•••HNC	0.0176	0.0465	0	1	0.245	0.0117	0.0136	-0.0115	-4.197
C_2H_2•••HCN	0.0117	0.0356	0.001	0.84	0.206	0.0065	-0.0091	-0.0063	-2.9682
C_2H_2•••HOH	0.0141	0.0409	0.001	0.93	0.224	-0.0163	-0.0113	-0.0036	-2.0925
C_2H_2•••HCCH	0.0103	0.0326	0.001	0.81	0.195	0.022	0.0095	-0.0117	-2.3836
Chlorine bond									
CH_3•••ClF	0.0266	0.0641	-0.002	1.13	0.192	-0.145	-0.289	-0.149	-3.909
CH_3•••ClCN	0.0069	0.0265	0.001	0.74	0.121	0.015	-0.14	0.019	-1.727
CH_3•••ClNC	0.0138	0.0424	0.001	0.93	0.153	-0.02	-0.239	-0.025	-3.191
CH_3•••ClCCH	0.0065	0.0231	0.001	0.75	0.124	0	-0.268	-0.007	1.373
CH_3•••ClOH	0.0117	0.0419	0.001	0.86	0.131	0.026	-0.074	0.025	-6.169
NH_3•••ClF	0.0687	0.1422	-0.016	1.32	0.25	-0.213	-0.323	-0.415	-8.301
NH_3•••ClCN	0.0145	0.0545	0.002	0.82	0.145	0.027	-0.236	-0.049	-2.654
NH_3•••ClNC	0.0263	0.1006	0.001	0.94	0.15	0.096	-0.059	0.03	-12.507
NH_3•••ClCCH	0.0115	0.0443	0.002	0.77	0.136	0.026	-0.267	-0.053	-1.988
NH_3•••ClOH	0.0284	0.0951	0	0.98	0.168	-0.011	-0.296	-0.151	-8.411
C_2H_2•••ClF	0.0238	0.0758	0	0.98	0.168	-0.15	-0.313	-0.221	-4.72
C_2H_2•••ClCN	0.0086	0.0332	0.002	0.72	0.128	0.005	-0.249	-0.015	-1.333
C_2H_2•••ClNC	0.0138	0.05	0.002	0.83	0.143	-0.011	-0.247	-0.044	-4.923
C_2H_2•••ClCCH	0.0076	0.0298	0.002	0.7	0.122	0.005	-0.279	-0.021	0.444
C_2H_2•••ClOH	0.0137	0.0502	0.002	0.83	0.14	-0.014	-0.308	-0.067	-4.804
C_2H_4•••ClF	0.0394	0.0917	-0.004	1.16	0.248	-0.208	-0.335	-0.274	-10.354
C_2H_4•••ClCN	0.0092	0.0321	0.002	0.74	0.147	0.003	-0.248	-0.008	-1.435
C_2H_4•••ClNC	0.0162	0.0516	0.001	0.88	0.171	-0.02	-0.248	-0.045	-5.982
C_2H_4•••ClCCH	0.0083	0.0309	0.002	0.7	0.131	-0.003	-0.165	-0.014	-2.73
C_2H_4•••ClOH	0.0175	0.0558	0.001	0.9	0.172	-0.023	-0.309	-0.073	-6.994
H_2•••ClF	0.0106	0.0429	0.002	0.82	0.137	-0.107	-0.268	-0.154	2.128
H_2•••ClCN	0.0046	0.0197	0.001	0.66	0.127	0.002	-0.222	-0.008	0.892
H_2•••ClNC	0.0069	0.0289	0.002	0.74	0.132	0	-0.216	-0.015	-0.698
H_2•••ClCCH	0.0042	0.0183	0.001	0.65	0.123	0.002	-0.248	-0.012	1.657
H_2•••ClOH	0.0067	0.0282	0.001	0.75	0.129	-0.004	-0.275	-0.032	-0.131

[*] ρ is the electron density, $\nabla^2\rho$ is Laplacian of electron density, H is the total energy density which is the summation of density of potential energy 'V' and Lagrangian form of kinetic energy density 'G', λ1 and λ3 are the curvature values, all at intermolecular BCP. N(X) is the average number of electronic charge on atom X, K(X) is the energy of atom X, Mu is the dipole moment of atom X and Vol is the volume of atom X. 'diff.' is difference between complex to the monomer for the mentioned properties.

Table 3. Percentage contributions of various resonance structures (See figure 8), covalency and ionicity for A•••X bond, D-X bond in complex and D-X bond from NBO Calculations

Complex	Weight (%)				Complex (X•••A bond) Structure 3		Complex (D-X bond) Structure 1+ Structure 2		Monomer (D-X bond)	
D-X•••A	Structure 1	Structure 2	Structure 3	Structure 4	%Covalency	%Ionicity	%Covalency	%Ionicity	%Covalency	%Ionicity
F-H•••NH_3	--	95.13	3.3	1.57	0.15	3.15	35.29	59.84	42.97	57.03
Cl-H•••NH_3	--	93.93	3.91	2.15	0.2	3.71	59.07	34.86	72.55	27.45
Br-H•••NH_3	--	92.53	4.89	2.57	0.31	4.59	62.65	29.89	79.78	20.22
F-Li•••NH_3	96.64	1.44	1.91	--	0.03	1.88	0.02	98.07	0	100
Cl-Li•••NH_3	93.75	4.01	2.25	--	0.05	2.19	0.19	97.56	0.09	99.91
Br-Li•••NH_3	92.74	4.87	2.4	--	0.06	4.56	0.3	97.3	0.16	99.84
F-Cl•••NH_3	--	68.92	29.3	1.78*	6.82	25.4	36.31	33.25	62.22	37.78

* 1.78% is the collective weight of six resonance structures all of which involve N•••Cl bond formation at the expense of the three N-H bond in NH_3.



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