

Ab initio and AIM theoretical analysis of hydrogen-bond radius of HD (D = F, Cl, Br, CN, HO, HS and CCH) donors and some acceptors†

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Recently, we defined 'hydrogen-bond radii' for various hydrogen-bond donors, DH where D = F, Cl, Br, CN, HO or CCH from an empirical analysis. It was shown that the A...H distances in B...HD complexes could be written as a sum of hydrogen bond radius for DH and a constant acceptor radius for A, which is the bonding atom/centre in B. This manuscript reports the determination of the hydrogen-bond radii for these molecules and H₂S from *ab initio* and atoms in molecules (AIM) theoretical calculations. The results from *ab initio* calculations are consistent with the empirical estimates for the six molecules noted above and provide the first estimate for hydrogen bond radius (1.08 ± 0.16 Å) for H₂S donor. The results from AIM theoretical analysis are in qualitative agreement with *ab initio* results. However, AIM analysis indicates that both hydrogen bond donor and acceptor radii vary in a systematic way from the strong to weak hydrogen bonds. Irrespective of the method used, the hydrogen bond donor radius increases in the order HF < HCl < H₂O < HBr < HCN < HCCH < H₂S, but mostly lie between Pauling's covalent and van der Waals radii of H atom. Interestingly, the acceptor radii for A in A...HD also increase in the same order. The AIM theoretical results on about 100 complexes have been reduced to suggest radii for H, F, O, N, C and S that are appropriate for strong, medium and weak hydrogen bonds. It is suggested that the use of a single van der Waals radius for D, H or A in determining the presence/absence of D-H...A hydrogen bonding be discontinued.

I. Introduction

The nature of chemical bonding, the interaction between atoms within a molecule, is fairly well understood.¹ However, our understanding of intermolecular interactions is still evolving.² Hydrogen-bonding is one of the intermolecular interactions, all of which could be classified as van der Waals interactions, following the equation named after him. The van der Waals constant *a* accounts for intermolecular attraction *i.e.* it does not stand for dispersive forces or electrostatic forces or hydrogen bonding. However, intermolecular interactions are widely classified as hydrogen bonding and van der Waals interactions. There has been a continuous^{3–7} and at times acrimonious,^{8,9} debate about whether a particular complex in the gas phase or a contact in the condensed phase should be classified as hydrogen bonding or van der Waals interactions from 1935³ (may be even earlier) to 2005.⁷ During these seven decades, the boundary has been continuously changing. Hydrogen bonding is, of course, of paramount importance in chemistry and biology.^{10–14} Initially it was observed between H, covalently bound to an electronegative atom X (N, O, F)

and another electronegative atom Y. It was usually represented as X-H...Y, where X-H is the hydrogen-bond donor and Y is the acceptor. It is represented as D-H...A in this work to highlight the fact that hydrogen bonding is no longer restricted to the most electronegative atoms, N, O or F. D-H is the hydrogen bond donor in which D and H are covalently bound and A is the acceptor atom/group in the acceptor molecule B. For example A could be the N atom and B could be the NH₃ molecule or A could be the C=C π center and B could be the C₂H₄ molecule. Hydrogen bonding by C-H and S-H groups are discussed in many of the books on hydrogen bonding.^{10–14} A large number of theoretical studies have been carried out by several groups and attempts have been made to unravel the nature of hydrogen bonding.^{15–20} Our work concentrates on one particular aspect in hydrogen bonding *i.e.* the distance between the H atom of DH and A. It does have some implications on what is hydrogen bonding and it will be discussed towards the end.

Pauling in his classic book¹ on the chemical bond discussed covalent, ionic and metallic bonds between atoms in a molecule/solid and also hydrogen-bonding and van der Waals interactions between molecules. He has defined covalent, ionic, metallic and van der Waals radii but not hydrogen-bond radius. It was not possible to get hydrogen positions with the X-ray diffraction data that Pauling mostly depended on and so it was not feasible at that time. However, today neutron diffraction data in the condensed phase and microwave spectroscopic data on hydrogen bonded complexes in the gas

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phase, can give reasonably accurate structural data. Locating H atom, especially within the accuracy of the other bonding radii (typically ± 0.1 Å for van der Waals or covalent radii) is possible. Still, Jeffrey in his recent book¹³ commented that “it is not possible to separate hydrogen-bond distances into hydrogen-bond atomic radii”. He pointed out one of the reasons to be that the hydrogen-bonding is a group-pair interaction and not an atom-pair interaction. The possibility of defining a hydrogen bond radius for various H bond donor groups (DH) has been overlooked. Pauling has, in fact, defined van der Waals radii for several groups in addition to the atoms. Though Jeffrey felt it was not possible to define a hydrogen bond radius, in the book he wrote with Saenger¹¹ they lamented the fact that van der Waals radii were still being used to confirm or rule out hydrogen bonding.

There is probably another reason why a hydrogen bond radius was not formulated earlier. Pauling showed that the distance between the two F^- in the strongly hydrogen bonded FHF^- is very close to the sum of the ionic radii of two F^- . This is not surprising given the fact that the bare proton is only 0.66 fm, five orders smaller than the unit of distance for Chemists, Å.²¹ Moreover, Buckingham and Fowler,¹⁸ somewhat fortuitously, found that the heavy atom distances in B:HF complexes were also close to the sum of their van der Waals radii, within ± 0.1 Å. This finding was somewhat unfortunate as well, as the H in HF is certainly not H^+ . Today, there are several experimental^{22,23} and theoretical²⁰ studies that support a partial covalent nature in H bonding. However, both Pauling and Buckingham had concluded that hydrogen is immersed in the electron cloud of the X atom in XH and the X–Y distances in X–H...Y hydrogen bond contacts are just the sum of van der Waals radii of X and Y, with hydrogen playing no role.

The books by Jeffrey and Saenger¹¹ and Desiraju and Steiner¹⁴ both point out the inadequacy of van der Waals radii of heavy atoms for identifying hydrogen bonding. If hydrogen bonding has to be either different from or a distinct subset of van der Waals interactions, shouldn't there be a hydrogen bond radius? We have shown recently^{24–27} that such a radius could be defined empirically for DH where D = F, Cl, Br, CN, OH, NH and CCH. This empirical analysis used experimental (microwave spectroscopy, X-ray and neutron diffraction results) H...A distances ($R_{H...A}$) in DH...A hydrogen bonds and the molecular electrostatic potential (MESP) of the isolated molecule B,²⁸ which has the atom or π center A that bonds to H from DH.

The usefulness of MESP in locating the sites of electrophilic attack^{29–31} is well established. The minima in the MESP are regions of large electron localization. An incoming electrophile, such as an electron deficient H in a hydrogen bond donor, approaches this minimum. The distance from the bonding atom A in B to the electrostatic minimum in B is denoted as $R_E(A)$. This $R_E(A)$ is close to, but not always identical to, the van der Waals radius of A.²⁸ This is taken as the contribution from A to the distance between A and H, $R_{H...A}$. Subtracting $R_E(A)$ from $R_{H...A}$ gives hydrogen bond radius of DH, denoted as $R_H(DH)$. Thus, $R_{H...A} = R_H(DH) + R_E(A)$. Gadre and Bhadane plotted $R_{H...A}$ vs. $R_E(A)$ for a series of B...HF complexes²⁸ and found it to be a straight line

with a slope close to 1. They took the intercept as van der Waals radius of H atom but found it to be less than 0.5 Å, significantly smaller than the accepted value of 1.2 Å.¹ Arunan and coworkers extended this analysis for a series of B...HD complexes (D = F, Cl, Br, CN, OH, NH and CCH).^{24–27} They plotted $R_{H...A} - R_E(A)$ vs. $R_E(A)$ and defined the intercept of this plot as the hydrogen bond radius. The slope was close to 0 for all series and it was fixed at 0 in determining the hydrogen bond radius. The hydrogen bond radii thus determined showed an inverse relation with dipole moment of the donor, extrapolating to the van der Waals radius of H atom at zero dipole moment. We note that Politzer and coworkers have recently used electrostatic potentials to define covalent radii for several atoms.^{32,33}

Since publishing these papers,^{24–27} we have come across a paper published in 1962 by Wallwork³⁴ that defined hydrogen bond radii for D–H groups in D–H...A contacts. He wrote the D...A distance as the sum of hydrogen bond radius for DH donor and A acceptor. He noted that the H bond radius of A was in fact close to the van der Waals radius of A, very much like the similarities between $R_E(A)$ and van der Waals radius of A. Wallwork, however, could not relate the hydrogen bond radius of DH to any of the physical properties of DH. Moreover, his analysis did not have the hydrogen atom positions for reasons pointed out earlier.

The objective of the present paper is two-fold. Firstly, the hydrogen bond radius could not be determined for H₂S in our earlier work,^{24–27} as accurate experimental data on B–H₂S complexes are scarce. Hydrogen bonding by SH group is important in the amino acid cysteine and its derivatives.^{11–14} Hence, it was decided to determine the hydrogen bond radius by *ab initio* calculations of a series of B–H₂S complexes. To test the validity of the *ab initio* results, calculations on the complete series of complexes with all donors were carried out as well. As will be shown later in the manuscript, there is reasonable agreement between the *ab initio* results and the earlier empirical results. Our second objective is towards testing the validity of $R_E(A)$ as contribution from A to the H...A distance. The $R_E(A)$ is a property of the isolated monomer. Hence, this approach neglects any change in the electron density distribution around the acceptor molecule B on hydrogen bond formation. It is consistent with the initial (should we now say outdated?) view of hydrogen bonding as primarily electrostatic interaction.¹ However, now it is well established that hydrogen bonding has contributions from several physical (electrostatic interactions between permanent and induced multipoles and dispersion forces) and chemical (covalent) forces.¹² Mutual penetration of electron density is, in fact, used as the necessary and sufficient condition for the presence of hydrogen bonding by Koch and Popelier.^{35,36} It was decided to use the atoms in molecules theoretical approach^{37,38} to determine hydrogen bond radii for the same donors. In this approach, the electron density topography of the complex is determined using the *ab initio* wave functions. The (3,–1) bond critical points (BCP, *i.e.* the point at which the electron density is minimum along the bond and maximum in the other two perpendicular directions) between H and A were located for the same series of complexes. The distance from the BCP to hydrogen, R_{H-X} (X is the bond critical point)

is defined as the hydrogen bond donor radius. The distance from the BCP to the acceptor atom/group A, $R_{A...X}$, is then the hydrogen bond acceptor radius which can be compared to $R_E(A)$. It is noted that the acceptor radius also increases when going from the strong (HF) to weak (H_2S) donors. The results are presented in this paper.

II. Computational methods

The geometries for about one hundred $B \cdots HD$ complexes ($D = F, Cl, Br, CN, OH, SH$ and CCH ; B has an atom or an electron rich region A that can accept a hydrogen bond), ~ 15 for each series, have been fully optimized at MP2(Full) level using 6-311++G** basis set. The level and basis sets were chosen with reliability and speed of calculations in mind, considering the large number of optimized structures. Frequency calculations at the same level have been done for all the optimized complex geometries to confirm the nature of the stationary points. For most of the complexes, the hydrogen-bonded structure is the global minimum. However for some complexes, the hydrogen-bonded structure is a local minimum, e.g. SO_2-H_2O . The hydrogen-bond distances, $R_{A...H}$, obtained from these optimized geometries have been used with the $R_E(A)$ of the corresponding bases, calculated at the same level, to obtain the hydrogen-bond radii. An average $R_H(DH)$ is obtained from the intercept of a plot of $R_{A...H}-R_E(A)$ versus $R_E(A)$, with the slope fixed at zero. Gaussian03 software package³⁹ was used for all the calculations. Atoms in molecule theoretical calculations were used to characterize the topological properties of the electron density and bond critical points (X) were located between H and A in each of the complexes. These calculations were done using the AIM2000 package.⁴⁰

It should again be mentioned here that our main emphasis is obtaining the intermolecular distances from calculations for determining the hydrogen-bond radii. Hence, no attempts

have been made to correlate the energetics to the distances or the vibrational frequencies, for the above complexes (though they could be readily obtained from the calculations). However, there are several reports where correlation between different properties of hydrogen-bond donor and acceptor are presented.⁴¹⁻⁴⁹

III. Results and discussions

III.1. Hydrogen-bond radii from *ab initio* calculations

The hydrogen-bond distances, $R_{A...H}$, for $B \cdots HD$ ($D = F, Cl, Br, OH, SH, CN$ and CCH) complexes and $R_E(A)$ for the monomer B, both from MP2(Full)/6-311++G** calculations, are listed in Table 1. The difference between them is the hydrogen bond radius, R_H , which has been listed in the table as well. The table has been arranged in the order of increasing $R_E(A)$. As is evident from the columns showing R_H for all donors, these values are approximately the same and do not have any obvious dependency on $R_E(A)$. This is illustrated better in the plot of $R_{A...H}-R_E(A)$ vs. $R_E(A)$ as shown in Fig. 1 (see also Fig. 7, later in the manuscript). These data were fit to straight lines with the slopes fixed at zero. The intercepts of these fitted lines give the average hydrogen bond radii for all the donors. The hydrogen bond radii determined from this analysis are 0.52 ± 0.04 (0.51 ± 0.09) Å, 0.74 ± 0.08 (0.70 ± 0.10) Å, 0.77 ± 0.05 (0.75 ± 0.09) Å, 0.78 ± 0.11 (0.77 ± 0.13) Å, 0.89 ± 0.05 (0.89 ± 0.12) Å, 1.01 ± 0.05 (1.07 ± 0.08) Å and 1.08 ± 0.16 Å for HF, HCl, H_2O , HBr, HCN, HCCH and H_2S , respectively. The numbers shown in parentheses are from the empirical analysis that used experimental distances and theoretical $R_E(A)$ values. The excellent agreement between these two estimates merely points out the reliability of MP2/6-311++G** calculations in predicting the geometry of the complexes, within the error limits quoted. It also indicates that the hydrogen bond radius predicted for H_2S should be

Table 1 Hydrogen-bond distances, $R_{A...H}$, for $B \cdots HD$ ($D = F, Cl, Br, OH, SH, CN$ and CCH) complexes and $R_E(A)$ for the monomer B, calculated at MP2/6-311++G** level of theory, in Å. A is the bonding atom/center in B

Acceptor B	Atom A	$R_E(A)$	HF		HCl		HBr		H_2O		H_2S		HCN		C_2H_2	
			$R_{A...H}$	R_H	$R_{A...H}$	R_H	$R_{A...H}$	R_H	$R_{A...H}$	R_H	$R_{A...H}$	R_H	$R_{A...H}$	R_H	$R_{A...H}$	R_H
H_2O	O	1.22	1.73	0.51	1.90	0.68	1.95	0.73	1.94	0.72	2.17	0.95	2.06	0.84	2.19	0.97
H_2CO	O	1.24	1.75	0.51	1.94	0.70	1.98	0.74	2.02	0.78	2.31	1.07	2.13	0.89	2.28	1.04
HF	F	1.30	1.87	0.57	2.08	0.78	2.16	0.86	2.11	0.81	—	—	2.16	0.86	2.27	0.97
H_3N	N	1.30	1.70	0.40	1.82	0.52	1.80	0.50	1.97	0.67	2.22	0.92	2.13	0.83	2.29	0.99
CH_3CN	N	1.34	1.83	0.49	2.03	0.69	2.09	0.75	2.10	0.76	2.35	1.01	2.20	0.86	2.35	1.01
SO_2	O	1.34	1.87	0.53	2.04	0.70	2.10	0.76	2.06	0.72	2.87	1.53	2.15	0.81	2.24	0.9
HCN	N	1.40	1.88	0.48	2.10	0.70	—	—	2.16	0.76	2.42	1.02	2.26	0.86	2.41	1.01
N_2O	O	1.41	2.00	0.59	2.23	0.82	2.29 ¹	0.88	—	—	—	—	2.32 ²	0.91	2.42 ³	1.01
CO_2	O	1.44	2.00	0.56	2.22	0.78	—	—	—	—	—	—	2.29	0.85	2.40	0.96
OC	C	1.60	2.12	0.52	2.42	0.82	—	—	2.46	0.86	2.77	1.17	2.58	0.98	2.71	1.11
N_2	N	1.60	2.13	0.53	2.37	0.77	2.46	0.86	2.37	0.77	—	—	2.46	0.86	2.60	1.00
C_3H_6	— ^a	1.61	2.14	0.53	2.34	0.73	2.38	0.77	2.42	0.81	2.64	1.03	2.52	0.91	2.62	1.01
C_2H_2	— ^a	1.62	2.18	0.56	2.43	0.81	2.50	0.88	2.44	0.82	2.68	1.06	2.59	0.97	2.69	1.07
C_2H_4	— ^a	1.64	2.20	0.56	2.43	0.79	2.49	0.85	2.45	0.81	2.70	1.06	2.63	0.99	2.72	1.08
H_2S	S	1.80	2.32	0.52	2.54	0.74	2.58	0.78	2.58	0.78	2.84	1.04	2.69	0.89	2.79	0.99
$\langle R_H \rangle$				0.52 ± 0.04		0.74 ± 0.08		0.78 ± 0.11		0.77 ± 0.05		1.08 ± 0.16		0.89 ± 0.05		1.01 ± 0.05

^a This is the C–C bond mid-point; superscripts indicate the optimized geometries that are not true minima but first order saddle points and the imaginary frequencies of the corresponding complex are: (1) 23.6i cm^{-1} . (2) 10.9i cm^{-1} . (3) 21.8i cm^{-1} . The last row gives the average hydrogen bond radius for the donor.

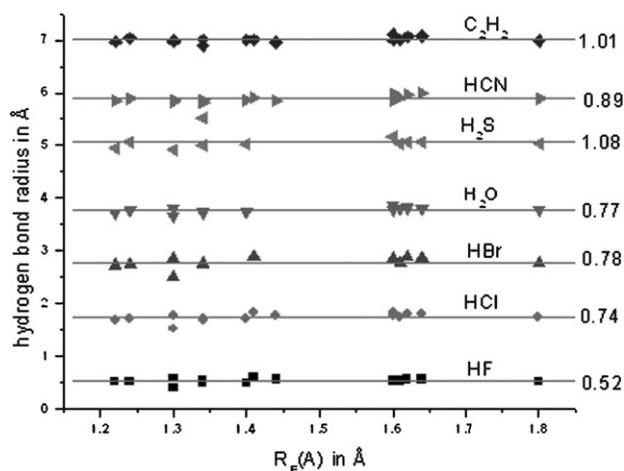


Fig. 1 Plot of the hydrogen bond radius $R_H(DH)$ ($=R_{A...H}-R_E(A)$) vs. $R_E(A)$ and their linear fits for HF, HCl, HBr, HCN, H_2O , HCCH and H_2S complexes determined at MP2/6-311++G** level calculations. A constant (C) has been added to the Y values of the seven complexes for clarity; $C_{HF} = 0.0$, $C_{HCl} = 1.0$, $C_{HBr} = 2.0$, $C_{H_2O} = 3.0$, $C_{H_2S} = 4.0$, $C_{HCN} = 5.0$ and $C_{HCCH} = 6.0$. The intercept shown is the hydrogen bond radius for the donor.

reasonable. The hydrogen bond radius for H_2S is validated by the known experimental data for a few complexes *i.e.* $C_2H_4-H_2S$ ⁵⁰, H_2S-H_2S ,⁵¹ H_3N-H_2S ,⁵² $C_6H_6-H_2S$ ⁵³ and $OC-H_2S$,⁵⁴ the estimated radii being 1.26, 0.98, 1.04, 1.19 and 1.29 Å, respectively. These experimental values give an average radius of 1.15 ± 0.12 Å for H_2S , which is very close to the *ab initio* prediction. The weakest hydrogen bond donor in this list has a radius very close to the van der Waals radius of H atom, 1.2 Å.^{1,55}

Our earlier work had shown that the hydrogen bond radii for HF, HCl and HBr had a strong inverse correlation with the dipole moment of HX, with a correlation coefficient of nearly 1.²⁴ The extrapolated value for hydrogen bond radius at zero dipole moment was 1.0 ± 0.1 Å, which is very close to the value determined for HCCH and H_2S . However, these molecules have significant non-zero bond dipole moments.⁵⁶ The dipole moments of the seven donors used in this study are given in Table 2. For H_2O , H_2S , HCN and HCCH, bond

Table 2 Dipole moment of H–D bond for different hydrogen-bond donors (HD)

D	Dipole moment/Debye ^a	Ref.
F	1.82	57
Cl	1.08	57
Br	0.78	57
I	0.45	57
$C \equiv N$	1.13	58
HO	1.51	57
HS	0.70	57
$C \equiv CH$	0.94	59
$HC=CH_2$	0.69	59

^a For the diatomic molecules, experimental dipole moments are given. For polyatomic molecules, bond dipole moments have been derived from experimental/theoretical approaches as outlined in the references.

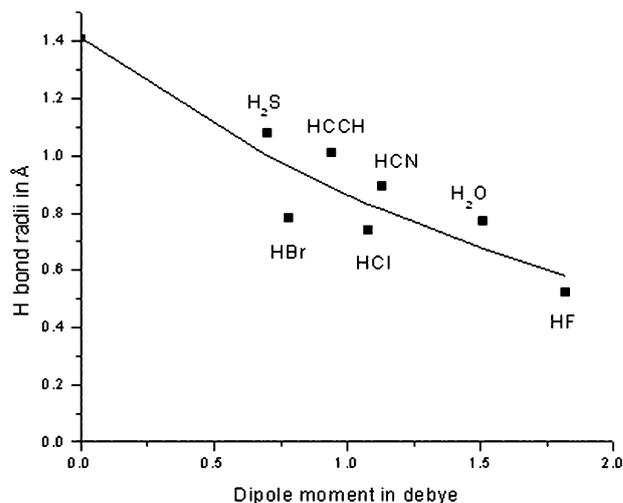


Fig. 2 Plot of the hydrogen bond radii for different hydrogen-bond donors (HX) against the H–X bond moment. Dipole moments have been taken from the literature (see Table 2) and the hydrogen bond radii have been calculated at MP2/6-311++G** level. The line shows an exponential fit extrapolating to 1.41 Å at zero dipole moment.

dipoles are listed. A plot of hydrogen bond radius vs. dipole moments for the seven donors is shown in Fig. 2. It is clear that the hydrogen bond radius increases with decreasing dipole moment. However, there is no linear relationship. Moreover, these data could not be fitted to any functional form with acceptable correlation coefficients. An exponential fit is shown simply as a guide line in Fig. 2 and has a correlation coefficient of 0.66. Moreover, it predicts a hydrogen bond radius of 1.41 Å for the zero-dipole limit, which is significantly larger than the van der Waals radius of H atom as the extrapolation shows? In fact, this is getting closer to the ionic radii of hydride ion, 1.54 Å,²¹ which is unrealistic. Linear fit (not shown) predicts the zero-dipole radii to be relatively smaller at 1.25 Å and the correlation coefficient is slightly smaller as well, 0.63.

Does our empirical analysis really lead to hydrogen bond radius for some donors larger than the accepted van der Waals radius of H atom as the extrapolation shows? In order to verify this, it was decided to look at ‘hydrogen bond donors’ with even lower bond dipole moment than the donors listed above, such as C_2H_4 and C_2H_6 . Experimental data on these complexes are not available. Geometries of ‘hydrogen bonded’ complexes with C_2H_4/C_2H_6 as donors and H_2O/HF as acceptors were fully optimized at the MP2(Full)/6-311++G** level. For the C_2H_4 complexes, the $H \cdots A$ ($A = F/O$) distances are 2.51 and 2.42 Å, respectively. The $C-H \cdots A$ geometry is nearly linear and the angles are 176 and 179°, respectively. These distances lead to hydrogen bond radius for C_2H_4 as 1.21 and 1.20 Å, respectively. For the corresponding C_2H_6 complexes, the $H \cdots A$ distances are 2.62 and 2.56 Å and the angles are 171 and 162°, respectively. The hydrogen bond radii for ethane from the two complexes are 1.32 and 1.34 Å, respectively. Clearly, the hydrogen bond radii for C_2H_4 and C_2H_6 are larger than the van der Waals radius of H atom according to this analysis. This observation led us to question our assumption of using constant $R_E(A)$ for the acceptors, irrespective of the

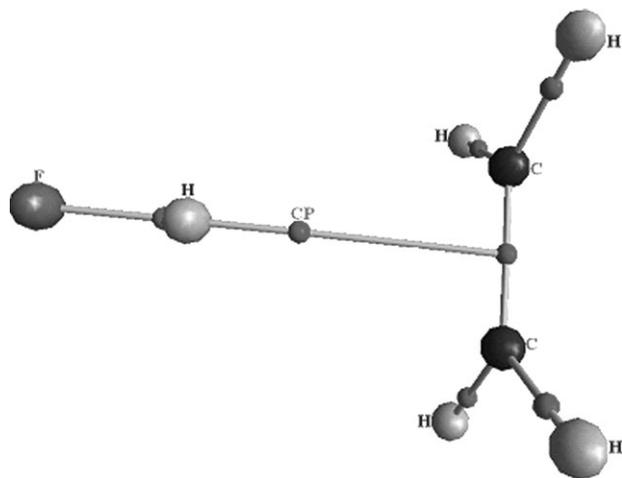


Fig. 3 The structure of C_2H_4-HF complex optimized at MP2/6-311++G** level. Bond critical points (BCP) have been calculated by the AIM theoretical method and these are shown in between all the atoms that are bonded. There is a BCP between the π centre in C_2H_4 and the H in HF. The distance between this BCP and the H in HF gives an estimate of the hydrogen bond radii of HF.

donors. It was decided to use atoms in molecules (AIM) theoretical calculations on the complexes to look for bond critical points between H and A. The advantage of these calculations is that the change in electron density around the monomers is already taken care off. Moreover, AIM theory could provide an independent theoretical basis for the hydrogen bond radius. The results are presented next.

III.2. Hydrogen-bond radii from AIM calculations

The AIM calculations were done using the *ab initio* wave functions calculated at MP2 (Full)/6-311++G** level. Bond critical points of the right topology (3,-1) could readily be observed between the H and the A atom/centre for all the complexes reported in Table 1. The structure and bond critical

points from AIM calculations are shown in Fig. 3, for a representative complex C_2H_4-HF . The distances from the BCP to H atom and A (R_{H-X} and R_{A-X}) are both listed in Table 3. The average of R_{H-X} for a given donor can be related to the hydrogen bond radius for that donor and R_{A-X} to the $R_E(A)$ from *ab initio* calculations. The scatter in R_{H-X} indicates how useful this parameter could be. The hydrogen bond radii determined by this method are 0.65 ± 0.07 Å, 0.78 ± 0.09 Å, 0.78 ± 0.08 Å, 0.81 ± 0.11 Å, 0.85 ± 0.08 Å, 0.92 ± 0.07 Å and 0.97 ± 0.13 Å for HF, HCl, H_2O , HBr, HCN, HCCH and H_2S , respectively. As is evident from the error limits, the scatter is about ± 0.1 Å for all donors. A comparison of hydrogen bond radii determined from empirical, *ab initio* and AIM analysis is shown in Table 4. The AIM results predict hydrogen bond radii for all donors to be in the range of 0.6 to 1.0 Å, compared to the *ab initio* prediction of 0.5 to 1.1 Å. Exponential fit of the AIM radii vs. dipole moment of the donor, Fig. 4, has a moderately larger correlation coefficient of 0.72 compared to the fit of *ab initio* results (0.66). Moreover, the extrapolation to zero dipole moment yields a more reasonable 1.12 Å unlike that of *ab initio* results that gave 1.41 Å. A linear fit (not shown) gives the zero-dipole radii as 1.07 Å with a correlation coefficient of 0.70. Finally, for the C_2H_4-HF , $C_2H_4-H_2O$, C_2H_6-HF and $C_2H_6-H_2O$ complexes, AIM analysis leads to R_{H-X} values of 1.04, 0.94, 1.11 and 1.02 Å, respectively.

It is clear that the AIM analysis leads to hydrogen bond radii below 1.2 Å for even the weakest of donors. For the strongest donor HF, the AIM radius is larger than the *ab initio* estimate and for the weak donors HCN, C_2H_2 and H_2S , the AIM radius is smaller than that from *ab initio* results. For the medium donors HCl, H_2O and HBr, the AIM radii are larger than, but within the error limits, of *ab initio* radii. It should be remembered that the $A \cdots H$ distance is the same in both *ab initio* and AIM analysis and that it is taken from the *ab initio* optimized structure. The fact that HF has a larger radius from AIM calculations implies that the H in HF is penetrating into the electron cloud of acceptor significantly. This leads to the

Table 3 Distances (in Å) $R_{H \cdots X}$ and $R_{A \cdots X}$ from AIM theoretical calculations. Last row shows the average $R_{H \cdots X}$ for all donors, which are the hydrogen bond radii for the donors from AIM calculations^a

Acceptor	HF		HCl		HBr		H_2O		H_2S		HCN		C_2H_2	
	$R_{H \cdots X}$	$R_{A \cdots X}$												
H_2O	0.55	1.18	0.65	1.25	0.68	1.27	0.67	1.27	0.81	1.36	0.74	1.32	0.81	1.39
H_2CO	0.56	1.19	0.68	1.26	0.70	1.28	0.72	1.30	0.89	1.42	0.77	1.36	0.86	1.42
HF	0.65	1.23	0.78	1.30	0.83	1.33	0.79	1.33	—	—	0.83	1.33	0.89	1.39
H_3N	0.50	1.20	0.58	1.24	0.57	1.23	0.65	1.32	0.79	1.44	0.72	1.40	0.80	1.49
CH_3CN	0.58	1.25	0.70	1.33	0.74	1.35	0.73	1.37	0.88	1.47	0.78	1.41	0.86	1.49
SO_2	0.63	1.24	0.74	1.30	0.78	1.32	0.74	1.31	1.28	1.63	0.80	1.35	0.85	1.39
HCN	0.60	1.28	0.74	1.36	—	—	0.76	1.40	0.92	1.50	0.81	1.44	0.89	1.51
N_2O	0.69	1.32	0.87	1.36	0.91	1.37	—	—	—	—	0.91	1.40	0.98	1.44
CO_2	0.69	1.30	0.85	1.37	—	—	—	—	—	—	0.88	1.41	0.94	1.46
OC	0.69	1.43	0.87	1.56	—	—	0.87	1.59	1.07	1.69	0.94	1.64	1.01	1.70
N_2	0.72	1.41	0.89	1.48	0.94	1.52	0.87	1.50	—	—	0.93	1.54	1.01	1.60
C_3H_6	0.71	1.47	0.84	1.53	0.87	1.49	0.86	1.48	1.00	1.66	0.91	1.60	0.97	1.66
C_2H_2	0.72	1.46	0.87	1.56	0.92	1.58	0.86	1.58	1.02	1.66	0.94	1.65	0.99	1.70
C_2H_4	0.73	1.46	0.88	1.55	0.92	1.57	0.87	1.58	1.04	1.67	0.96	1.68	1.01	1.71
H_2S	0.69	1.63	0.83	1.72	0.85	1.73	0.83	1.75	0.99	1.85	0.89	1.80	0.94	1.85
$\langle R_{H \cdots X} \rangle$	0.65 ± 0.07		0.78 ± 0.09		0.81 ± 0.11		0.78 ± 0.08		0.97 ± 0.13		0.85 ± 0.08		0.92 ± 0.07	

^a The last row gives the average R_{H-X} , that can be compared to the hydrogen bond radius for the donor. See Table 4.

Table 4 'Hydrogen-bond radii' of different HX^a

Donor	Empirical	<i>Ab initio</i>	AIM	AIM limit ^b
HF	0.51 ± 0.09	0.52 ± 0.04	0.65 ± 0.07	0.73
HCl	0.70 ± 0.10	0.74 ± 0.08	0.78 ± 0.09	0.89
H ₂ O	0.75 ± 0.09	0.77 ± 0.05	0.78 ± 0.08	0.87
HBr	0.77 ± 0.13	0.78 ± 0.11	0.81 ± 0.11	0.94
HCN	0.89 ± 0.12	0.89 ± 0.05	0.85 ± 0.08	0.96
HCCH	1.07 ± 0.08	1.01 ± 0.05	0.92 ± 0.07	1.01
H ₂ S	—	1.08 ± 0.16	0.97 ± 0.13	1.07
DH ^{0c}	—	1.41	1.12	1.26

^a Empirical analysis was carried out for HF, HCl, HBr, HCN, H₂O and HCCH, taking experimental $R_{A...H}$ and the $R_E(A)$ values from MP2/6-311++G** level calculation. *Ab initio* analysis was carried out with both $R_{A...H}$ and $R_E(A)$ values from calculation. AIM analysis gives the distance from H to the bond critical point between H and A. ^b Maximum hydrogen bond radius calculated within the series of complexes considered in this work. As evident from Fig. 7, the hydrogen bond radius approaches a limit for all donors. ^c Hydrogen bond radii for a hypothetical donor with zero dipole moment. This estimate is from an exponential decay fit of the radius vs. dipole moment, extrapolated to zero dipole moment.

reduction in acceptor radius compared to $R_E(A)$ used for *ab initio* analysis. For HCl, H₂O and HBr, the extent of penetration is within the error limits of the radii quoted. For the weak donors, HCCH, HCN and H₂S, the acceptor radii are obviously larger than $R_E(A)$. Clearly, the acceptor radius is increasing as the donor changes from the strongest HF to the weakest H₂S in this list. The donor radii also increase in this order, irrespective of the method used, as evident from Table 4. A closer scrutiny of Table 3 clearly shows this and the details are discussed next.

For comparison, Table 3 lists the acceptor in the same order as Table 1. However, unlike in Table 1, the hydrogen bond radius (R_{H-X} in Table 3) shows a general increase as we go down the columns and then levels off. The data in Table 3 were plotted in different ways to look for trends. Fig. 5 shows a global plot of R_{H-X} against R_{A-X} for all the complexes investigated. It suggests that R_{H-X} increases with R_{A-X} , in general. However, all the points corresponding to H₂S as acceptor were distinctly different in the plot and they appear at the lower-right half. This led us to two important conclusions. First, for the same acceptor and different donors, there is a good correlation between R_{H-X} (donor radius) and R_{A-X}

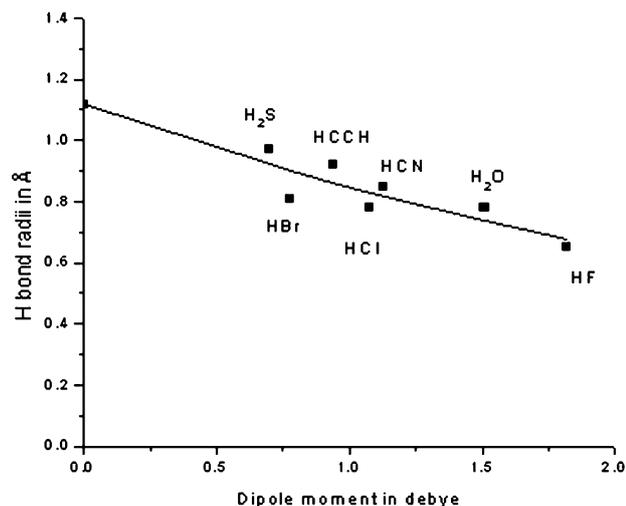


Fig. 4 Same as Fig. 2, except that the hydrogen bond radii are from AIM calculations. The extrapolation to zero dipole gives 1.12 Å.

(acceptor radius). It was decided to look at this correlation for similar acceptors. The acceptors were grouped based on the atom/centre that forms the hydrogen bond. Fig. 6 shows the correlation between hydrogen bond donor and acceptor radii for all complexes with O atom as the acceptor (H₂O, H₂CO, CO₂, N₂O and SO₂). The correlation coefficient is very good at 0.975. Similarly, the data for all complexes with N atom as acceptor (NH₃, HCN and CH₃CN, correlation coefficient = 0.978) and π acceptors (C₂H₄, C₂H₂ and C₃H₆, correlation coefficient = 0.912) also show very good correlation (figures not shown). The other three acceptors HF, H₂S and CO have unique acceptor atoms and they also showed similar correlation, individually. As the hydrogen bond becomes weaker, both the donor and acceptor radii are increasing.

The second important observation from Fig. 5 is that the complexes with H₂S as acceptor appear to have a smaller hydrogen bond radius than what would be implied by a simple extrapolation of data shown in the figure. The hydrogen bond radius from AIM calculations is clearly approaching a limit, as

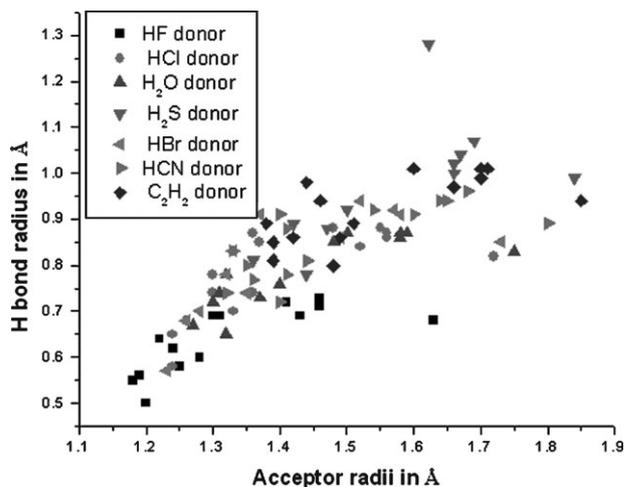


Fig. 5 Global plot of all R_{H-X} (equivalent to hydrogen bond donor radius) vs. R_{A-X} (acceptor radius) for all the complexes investigated. The seven points at the lower right half are from H₂S as acceptor. In general, for a given acceptor such as H₂S, both donor and acceptor radii increase as the hydrogen bond becomes weaker, see Fig. 6.

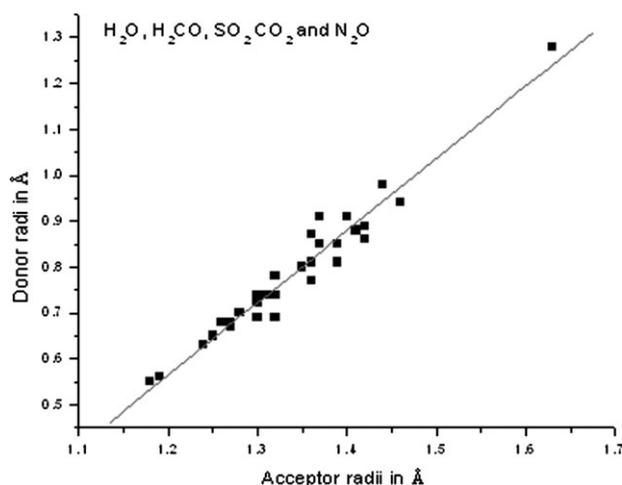


Fig. 6 Same as Fig. 5, but restricted to all molecules having O atom as the acceptor (listed on top), with no restriction on donor. The correlation coefficient is 0.975.

already pointed out. Plots of hydrogen bond radii vs. $R_E(A)$ from *ab initio* and R_{A-X} from AIM calculations, for all the HF complexes considered here, show this difference clearly, see Fig. 7. For comparison, both plots are drawn with the same scale. This plot is representative for all the donors. While, *ab initio* results show only random variation, the AIM results show that the hydrogen bond radius increases initially as R_{A-X} increases and then plateaus. It appears to give a limiting value of hydrogen bond radius for every donor and this limiting value is below the van der Waals radius of H atom for all donors in this study. Table 4 includes this limiting value for all the hydrogen bond donors.

As already pointed out, the R_{A-X} for the acceptor from AIM calculations, is related to $R_E(A)$ for the monomer. Table 5 compares these two parameters. Here again, the average value of R_{A-X} found for the complexes with the seven donors is close to $R_E(A)$. It provides a rationale for the successful separation of R_{A-H} as the sum of a hydrogen bond donor radius and acceptor radius in our empirical/*ab initio* analysis. However, the AIM calculations suggest that the acceptor radius R_{A-X} increases when the donor changes from HF to H_2S . A plot of acceptor radius as a function of dipole moment of the donor is shown in Fig. 8 for several acceptors. Interestingly, for all these acceptors, the radii increase with the decrease in dipole moment of the donors. Somewhat intriguingly, the extent of increase is approximately the same for all acceptors *i.e.* linear fitting of acceptor radii vs. dipole moment of the donor yields a slope of about -0.14 for all the acceptors. The correlation coefficients of all these fits are about 0.7. For all 15 acceptors, it is clear from Table 3 that the acceptor radius increases by about 0.2 \AA for H_2S compared to HF. The acceptor radii could be grouped into three sets depending on the donors. For HF, the acceptor radius is the lowest. For HCl, HBr and H_2O as donors, the acceptor radius is approximately the same. Finally, for H_2S , HCCH and HCN, the acceptor radius is approximately the same. These three sets of radii are also included in Table 5, along with the limiting radii estimated by extrapolation to zero dipole moment (Fig. 8).

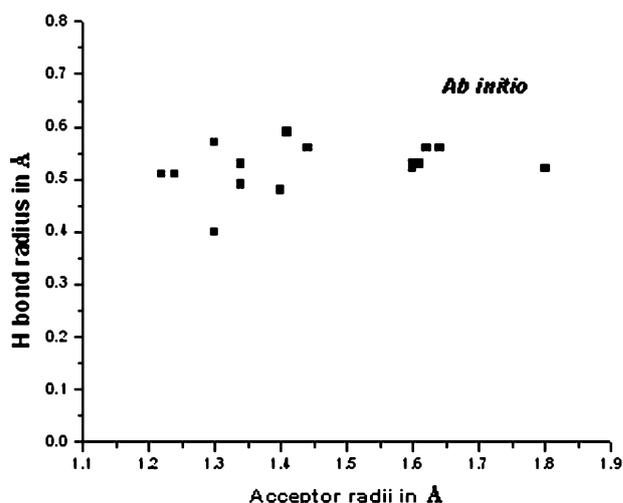
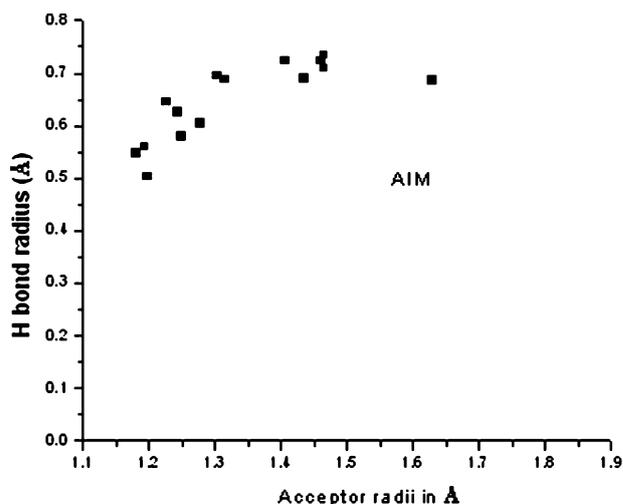


Fig. 7 Hydrogen bond radius from MP2 and AIM calculations as a function of acceptor radii, $R_E(A)$ from MP2 and R_{A-X} from AIM calculations, for all HF complexes investigated. The AIM calculations predict an initial increase followed by leveling off whereas the *ab initio* calculations show that the hydrogen bond radii vary randomly as acceptor radius increases. This is typical for all the donors considered in this work.

III.3. Distance criterion for hydrogen-bonding

Generally the criterion used for the existence of hydrogen-bonding is that the distance between the heavy atoms $R_{D...A}$ should be less than the sum of their van der Waals radii $[\sigma(D) + \sigma(A)]$.^{60–62} This is the default criterion for hydrogen-bonding given in the documentation for the Mercury software in Cambridge Crystal Structure Database.⁶³ However, there have been numerous reports of hydrogen-bonding at much longer distances. For instance, Desiraju and Steiner¹⁴ point out in their book that even a conservative C–O distance threshold of 3.25 or 3.3 \AA may still not be long enough to rule out the presence of C–H...O hydrogen-bonds. Although they have mentioned CH groups in general, we will take acetylenic CH group as an example. As seen from Table 2, the C–H bond dipole moment of HCCH is 0.94 D and is very close to that of

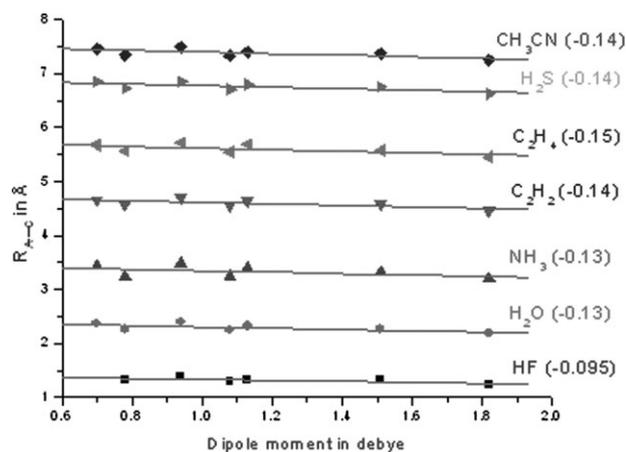


Fig. 8 The acceptor radius from AIM calculations plotted as a function of the dipole moment of the donor. Note that the linear fitting results in a nearly constant slope (-0.14) for all acceptors. Slope is indicated next to the lines. A constant value from 0 to 6 has been added to the Y values for the seven acceptors successively for clarity, similar to Fig. 1.

HCl (1.08 D). Hydrogen bonding by acetylenic group in the condensed phase or acetylene in the gas phase is well accepted. According to our definition of a hydrogen bond radius, for linear contact, the $C \cdots O$ distance for an acetylenic hydrogen bonded to a $C=O$ group can be estimated as follows:

$$R_{C-O} = R_{CH} + R_H(CH) + R_H(CO)$$

Here, R_{CH} is the $C-H$ single bond distance which could be taken approximately as 1.0 \AA . The hydrogen bond radius for HCCH group, $R_H(CH)$, is 1.0 \AA . The $R_H(CO)$ is the acceptor radius for $C=O$ group for the CH donor and is taken to be that of formaldehyde, 1.4 \AA , see Table 5. With these values, R_{C-O} is expected to be 3.4 \AA for a genuine hydrogen bonded contact. Although it has been realized for some time that the sum of van der Waals radii of heavy atoms can not be used for locating hydrogen bonds, our definition of a hydrogen bond radius gives a quantitative justification for the same. It is clear

that the $C \cdots O$ distance could be even longer if the $C-H$ group is less acidic. How longer could it be? For really weak hydrogen bonds, the hydrogen bond radius could approach 1.2 \AA and the acceptor radius could be slightly longer as well. Thus, one could expect hydrogen bonding interactions for $C \cdots O$ distances up to 3.6 \AA .

After completions of this work, we have come across a very recent paper by Klein which comes to a very similar conclusion.⁶⁴ Klein has used electron density at the critical points to suggest that the cutoff ‘van der Waals radii’ for the H, N and O atoms should be different for $X-H \cdots Y$ and $C-H \cdots Y$ ($X/Y = O/N$) hydrogen bonds. For $X-H \cdots Y$ contacts, he recommends 0.98 , 1.46 and 1.33 \AA for H, N and O atoms, respectively. For $C-H \cdots X$ contacts, he recommends the corresponding radii to be 1.18 , 1.66 and 1.50 \AA . These radii correspond to the distance from the nuclei to the point where electron density, ρ , is 0.005 au for $X-H \cdots Y$ and 0.002 au for $C-H \cdots X$. Klein has quoted 0.8 \AA as the H radius corresponding to an electron density of 0.010 au . He has used MPWPW91/6-311+G(2d,p) level of calculations to determine the electron density for N_2 , O_2 and H_2 molecules as reference. The electron densities at the critical points for all the complexes in this study are given in Table 6. For all the HF complexes, the electron densities at the BCP range from 0.0127 au ($N_2 \cdots HF$) to 0.0478 au ($H_3N \cdots HF$). Hence, for HF complexes, the cutoff for hydrogen bond radius for the donor should be less than 0.8 \AA . For HCl, HBr and H_2O complexes the lowest electron density at BCP is 0.008 au . Clearly for these complexes, a typical hydrogen bond radius should be less than 0.98 \AA and the maximum radius observed in these complexes is 0.94 \AA for $N_2 \cdots HBr$ (see Table 3). We agree with Klein that 0.98 \AA could well be a cutoff radius for H atom in these complexes. For H_2S and HCCH, the maximum hydrogen bond radius (R_{H-C}) has come out to be about 1.0 \AA in our analysis and the minimum electron density at BCP is 0.0056 au for $N_2 \cdots HCCH$. This is in excellent agreement with the result from Klein’s DFT calculations with a moderately larger basis set than what we have used. As pointed out earlier, for weak donors such as C_2H_4 , the cutoff in hydrogen

Table 5 Comparison of $R_E(A)$ for the monomers with R_{A-X} from AIM theoretical calculations^a

Acceptor	$R_E(A)$	$\langle R_{A-X} \rangle$	$R_{A-X}(1)$	$R_{A-X}(2)$	$R_{A-X}(3)$	R_{A-X}^0
H_2O	1.22	1.29 ± 0.07	1.18	1.26	1.36	1.43 ± 0.07
H_2CO	1.24	1.32 ± 0.08	1.19	1.28	1.40	
HF	1.30	1.32 ± 0.05	1.23	1.32	1.36	1.43 ± 0.05
H_3N	1.30	1.33 ± 0.10	1.20	1.26	1.44	1.48 ± 0.13
CH_3CN	1.34	1.38 ± 0.08	1.25	1.35	1.46	1.55 ± 0.08
SO_2	1.34	1.36 ± 0.12	1.24	1.31	1.37	
HCN	1.40	1.42 ± 0.08	1.28	1.38	1.48	
N_2O	1.41	1.38 ± 0.04	1.32	1.37	1.42	
CO_2	1.44	1.38 ± 0.06	1.30	1.37	1.44	
OC	1.60	1.60 ± 0.09	1.43	1.58	1.68	
N_2	1.60	1.51 ± 0.06	1.41	1.50	1.57	
* C_3H_6	1.61	1.55 ± 0.08	1.47	1.50	1.64	
* C_2H_2	1.62	1.60 ± 0.07	1.46	1.57	1.67	1.76 ± 0.07
* C_2H_4	1.64	1.60 ± 0.08	1.46	1.57	1.69	1.77 ± 0.09
H_2S	1.80	1.76 ± 0.07	1.63	1.73	1.83	1.91 ± 0.07

^a $\langle R_{A-X} \rangle$ is the average value for all seven donors. $R_{A-X}(1)$ is the acceptor radius for HF complexes; $R_{A-X}(2)$ is the average value from HCl, HBr and H_2O complexes and $R_{A-X}(3)$ is the average from HCN, HCCH and H_2S complexes. The last column gives the extrapolated value at zero dipole moment for R_{A-X} vs. dipole moment of the donor (see Fig. 8).

Table 6 Electron densities (in au) at the H-bond critical points for B...HD complexes calculated at MP2/6-311++G** level

B	HF	HCl	HBr	H ₂ O	H ₂ S	HCN	C ₂ H ₂
H ₂ O	0.0342	0.0254	0.0234	0.0218	0.0151	0.0172	0.0131
H ₂ CO	0.0334	0.0246	0.0232	0.0196	0.0126	0.0144	0.0121
HF	0.0189	0.0135	0.0118	0.0116	—	0.0107	0.0087
H ₃ N	0.0478	0.0400	0.0428	0.0261	0.0177	0.0199	0.0142
CH ₃ CN	0.0292	0.0206	0.0185	0.0163	0.0113	0.0134	0.0101
SO ₂	0.0212	0.0168	0.0156	0.0151	0.0050	0.0129	0.0106
HCN	0.0251	0.0174	—	0.0142	0.0098	0.0121	0.0089
N ₂ O	0.0154	0.0092	0.0087	—	—	0.0072	0.0059
CO ₂	0.0143	0.0105	—	—	—	0.0085	0.0071
OC	0.0171	0.0108	—	0.0089	0.0061	0.0075	0.0059
N ₂	0.0127	0.0094	0.0083	0.0084	0.0084	0.0074	0.0056
C ₃ H ₆	0.0185	0.0143	0.0137	0.0111	0.0090	0.0096	0.0080
C ₂ H ₂	0.0158	0.0114	0.0106	0.0102	0.0079	0.0081	0.0068
C ₂ H ₄	0.0158	0.0118	0.0111	0.0099	0.0079	0.0078	0.0066
H ₂ S	0.0193	0.0139	0.0134	0.0116	0.0084	0.0098	0.0082

bond radius can be taken as the van der Waals radius of H atom, 1.2 Å. However, it should be realized that the acceptor radius should be different for different donors. A single van der Waals radius can not be used either for the acceptor or the donor.

Results from Tables 4 and 5 could be grouped based on acceptor atoms to arrive at our final recommendations. These are given in Table 7 for H, O, N, F, C (π centre) and S atoms corresponding to strong (HF) medium (H₂O/HCl/HBr) and weak (HCN, HCCH and H₂S) hydrogen bonds. For strong hydrogen bonds, the acceptor radius should be about 0.2 Å less than its van der Waals radius and the radius of H atom should be significantly smaller in the range of 0.5–0.7 Å. For the medium hydrogen bonds, the acceptor radius is 0.1 Å smaller than van der Waals radius and the hydrogen radius is about 0.9 Å. For weak hydrogen bonds, the hydrogen radius is 1.1–1.2 Å and the acceptor radius is equal to or even larger than its van der Waals radius. The limits given in Table 7 for medium and weak hydrogen bonds are very close to the values recommended by Klein for OH and CH as donors.

Table 7 Recommended values for limiting radii (Å) for some atoms involved in strong, medium and weak hydrogen bonding^a

Atom	Strong	Medium	Weak	Limit ^b	Pauling
H	0.73	0.89	1.07	1.26	1.20
F	1.23	1.32	1.36	1.43	1.35
O	1.25	1.32	1.40	1.43	1.40
N	1.24	1.33	1.46	1.55	1.50
C ^c	1.46	1.55	1.67	1.77	1.70
C	1.43	1.58	1.68	1.77	
S	1.63	1.73	1.83	1.91	1.85

^a Strong hydrogen bonds involve HF as donor, medium hydrogen bonds include H₂O, HCl and HBr as donors and weak hydrogen bonds typically involve C–H and S–H as donors. Both the acceptor and donor radii should be different for these three groups. All acceptor atoms radii have been observed to increase by 0.2 Å from HF to H₂S. The radius of H atom varies over a much larger range. ^b These are extrapolated values at zero dipole moment of the donor and could be taken as an estimate for the van der Waals radius of these atoms. The last column gives the van der Waals radius recommended by Pauling. ^c Corresponds to π electron radius in CC acceptors. The penultimate row has the radii determined from CO as acceptor. It is interesting to note that both lead to very similar values.

It is worthwhile to consider the definition of a hydrogen bond at this point. Should one conclude that the nature of interactions is van der Waals, if the hydrogen bond radius for a donor approaches van der Waals radius of H atom and the acceptor radius approaches/exceeds its van der Waals radius? It appears that any such division based on a chosen limit in distance, binding energy, spectroscopic shifts *etc.*... would all be arbitrary. The hydrogen bond donor radius varies from the covalent to van der Waals radius of H atom continuously and we have “hydrogen bonding without borders” as Parthasarathy *et al.*⁴⁷ write in a recent paper. Blue-shifting hydrogen bonds are as real today as are the red-shifting hydrogen bonds.⁶⁵ The most celebrated difference between hydrogen bonding and van der Waals interaction is the directionality. As discussed above, the C₂H₄–H₂O complex has a geometry with directional C–H...O interaction. We had shown earlier that, for H...O distances up to 3.0 Å, the most preferred C–H...O angle is 180°, even when the C–H is from a H–CH₂–CH₂ group (no electronegative substituent in the primary C) based on the Cambridge Crystal Structure Database analysis.²⁷ However, these interactions would not qualify as a hydrogen bond according to definitions given in many sources. The definition given by Pimentel and McClellan¹⁰ is a good exception. According to them, “A hydrogen bond is said to exist when: (1) there is evidence of a bond and (2) there is evidence that this bond specifically involves a hydrogen atom already bonded to another atom”. With this definition along with the definition of a bond given by Pauling^{1,66} the isolated complexes of H₂S, HCCH, C₂H₄ and C₂H₆ in the gas phase are clearly hydrogen bonded *i.e.* they are all bound through an intervening H atom. In all these complexes, there is an electron deficient H atom already bonded to one atom, interacting with an electron rich region (either a lone pair or π pair in our examples) from another molecule. It is well established now that the acceptor could be an unpaired electron,⁶⁷ sigma bonding electrons⁶⁸ or hydride ion,⁶⁹ as well. One could extend the argument by adding rare gas atoms as regions of electron density,⁷⁰ and Ar–HF could be categorized as a hydrogen bonded complex following Bader.³⁷ Hydrogen bonding could then be defined as an attractive interaction between an electron deficient hydrogen atom already bonded to one atom and an electron rich region either within the same or with another

atom/molecule. This definition would cover all the known examples of hydrogen bonding interaction existing in the literature today.

4. Conclusions

Ab initio and AIM theoretical calculations at MP2/6-311++G** level have been used to determine the hydrogen bond donor radius for HF, HCl, H₂O, HBr, HCN, HCCH and H₂S. The *ab initio* results for the first six molecules are in reasonable agreement with earlier empirical estimates and provide the first estimate for H₂S. The hydrogen bond radii increase from HF to H₂S in the order HF < HCl < H₂O < HBr < HCN < HCCH < H₂S. The results from AIM theoretical analysis supports such a division of the A...H distances as the sum of hydrogen bond donor and acceptor radii. The radii determined from AIM method are in qualitative agreement with the *ab initio* results and predict the same order. However, AIM results show that the acceptor radii also increase in a B...HD complex as D changes from F to SH in the same order. Both the hydrogen-bond donor and acceptor radii have some inverse correlation with the H–D dipole moment. The AIM results from a comprehensive list of about 100 complexes have been reduced to suggest limiting radii for H, F, O, N, S and C atoms and carbon π centre that can be used for strong, medium and weak hydrogen bonding. For strong hydrogen bonds, the radii for both donor and acceptor are less than the accepted van der Waals radii of H and A. Our analysis also indicates that hydrogen takes its rightful place in determining the A–D distance in A...HD hydrogen bonds, unlike what has been assumed earlier.^{1,18} It is strongly recommended that the practice of using a single van der Waals radius for these atoms for determining the presence or absence of hydrogen bonding be discontinued.

Note added after completion

A recent paper published in the *Journal of the American Chemical Society* (M. Harigai, M. Kataoka and Y. Imamoto, 2006, **128**, 10646) is titled “A single CH/ π weak hydrogen bond governs stability and the photocycle of the photoactive yellow protein”. However, the authors point out that the C...C distance of 3.78 Å observed in their work is higher than the reported value of 3.5 Å for CH/ π interaction (no reference given). We note that the C...C distance can be predicted from the hydrogen bond radii reported in this paper as follows:

$$\begin{aligned}R_{C-C} &= R_{CH} + R_H(CH) + R_H(C) = 1.0 + 1.1 + 1.7 \\ &= 3.8 \text{ \AA}\end{aligned}$$

Clearly, the distance reported is within reasonable limits.

Acknowledgements

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