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Is there a hydrogen bond radius? Evidence from microwave spectroscopy, neutron scattering and X-ray diffraction results†

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Intermolecular distances in D–H···A hydrogen bonded systems have usually been interpreted in terms of the van der Waals radii of D and A. In this work, X-ray and neutron diffraction data from the Cambridge Crystal Structure Database (CSD) and the electrostatic potential of A, have been used to define hydrogen bond radii for OH, NH and CH groups. For OH, X-ray and neutron diffraction both give comparable results, validating the X-ray data for defining a hydrogen bond radius. The hydrogen bond radii determined for C≡CH and OH groups from CSD analysis are comparable to those determined from the gas phase rotational spectroscopic data for HCCH and H_2O complexes. For NH as a proton donor, gas phase structural data are scarce and a hydrogen bond radius has been determined by using X-ray diffraction data only. For the CH group, the histogram of hydrogen bond distances shows a peak recognizable as a hydrogen bond only if it is acidic such as CCl_3H, OCH (aldehydic) or CCH (acetylenic). The hydrogen bond radii for OH, NH and acidic CH groups are 0.60 ± 0.15, 0.76 ± 0.15 and 1.10 ± 0.20 Å, respectively. For C–CH_3 and CH_2CH_3, though a peak in the histogram of distances is not found, the distribution of hydrogen bond angles unambiguously shows that the preferred geometry is linear. It appears that a CH group without any electronegative substituents could have a radius larger than 1.2 Å when involved in hydrogen bonding.

Introduction

Hydrogen bonding has fascinated chemists and biologists for close to a century now (see refs. 1 and 2 for the history). It is clear that hydrogen bonding was already postulated[3–5] even when Langmuir[6] and Lewis[7] were defining covalent bonding as the sharing of two electrons by two atoms. Pauling, in his seminal book[8] discussed covalent, ionic and metallic bonds within a molecule and also hydrogen bonding and van der Waals interactions between molecules. Extensive analysis of the bond distances in molecules and crystals led him to define covalent, ionic, metallic and van der Waals radii for several atoms. A hydrogen bond radius was not defined. There must have been several good reasons for this. The most important one could be that the accurate location of hydrogen was very difficult with the then available X-ray crystallographic data, which Pauling mostly depended on. Moreover, unlike other bonds that involve only two atoms, at least three atoms are involved in hydrogen bonding, making it impossible to define a unique hydrogen bond radius for different atoms. The original definition of a hydrogen bond invoked two electronegative atoms (D and A) in addition to the hydrogen atom, D–H···A. Pauling did define van der Waals radii for several groups including CH_3, CH_2 and the benzene ring. Could one define a hydrogen bond radius for various H-bond donor groups D–H such as O–H and N–H? Moreover, today there is no such restriction on the electronegativity of the atoms and there are several examples of hydrogen bonding involving C–H and S–H groups as donors and π systems as acceptors.[1,2,9] Since there are no restrictions on the electronegativity of the groups, could one estimate the radii for S–H and C–H groups as well?

Jeffrey and Saenger in their book,[9] lament the fact that D—A distances are compared to the sum of van der Waals radii of D and A for determining the presence of hydrogen bonds. This neglects the fact that D—A distance should be the vectorial sum of the D–H covalent bond distance and H···A hydrogen bond distance. The default criterion given in the documentation for Mercury software in CSD is that the D—A distance be less than the sum of their van der Waals radii.[10] On the other hand Desiraju and Steiner[2] in their recent book point out that even a conservative C—O distance threshold of 3.25 or 3.3 Å may still not be long enough to rule out the presence of C–H···O hydrogen bonds. In this work, the D—A distance (corrected for the D–H–A angle) for a D–H···A hydrogen bond is defined following Jeffrey and Saenger as:

$$R_{D—A} = R_{D–H} + R_{H\cdots A} \quad (1)$$

Here, $R_{D–H}$ is the covalent bond distance D–H and $R_{H\cdots A}$ is the distance between H and A. Further, the $R_{H\cdots A}$ distance is written as a sum of the hydrogen bond radius of DH and the radius of A determined by the minimum in the electrostatic potential of A *i.e.*

$$R_{H\cdots A} = R_H\,(DH) + R_E(A) \quad (2)$$

It turns out that R_E(A) is close to the van der Waals radius of A. It is shown, in this manuscript, that for a typical CH group forming a hydrogen bond, eqns. (1) and (2) lead to an $R_{C—O}$ distance of 3.6 Å (R_{CH} = 1.1 Å, R_H(CH) = 1.2 Å and R_O = 1.3 Å) for linear geometry, justifying the assertions of Desiraju and Steiner for a longer cutoff.

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† Electronic supplementary information (ESI) available: summary of database analysis (Table S1 and S2), MESP topological and geometric parameters for substituted pyridines (Table S3) and carbonyls (Table S4), histograms of hydrogen bond distances for various H bond donors with pyridinic(N) as acceptor (Fig. S1) and a typical search routine used for retrieving data from the CSD. See http://www.rsc.org/suppdata/nj/b4/b411815d/

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Background

Buckingham and Fowler, in a classic paper,[11] used electrostatic potentials to explain and predict the radial and angular geometries for a series of hydrogen bonded complexes. In their model, 'point multipoles were assigned to atoms and embedded in hard spheres to represent short range repulsions'. They noted that, for a series of FH···A complexes, the distance between the F and A was very close to the sum of the van der Waals radii of F and A, within ±0.1 Å. This follows the explanation given by Pauling for the hydrogen bond in FHF^- where two F^- interact with H^+ (see Fig. 12.1 in Pauling's book[8]). The bare proton with no electron shell around it, has a radius of merely 0.66 fm,[12] and is of no dimensional consequence for chemistry or biology. However, in the HF···HF dimer, despite the electronegativity difference between F and H, hydrogen is not H^+. Neglecting the H in a typical hydrogen bond does not appear to be reasonable. Not surprisingly, for the series of ClH···A and BrH···A, the difference between the Cl/Br—A distance and the sum of their van der Waals radii was positive *i.e.* ±0.2 Å to ± 0.3 Å.[13]

Gadre and Bhadane looked at the H···A distances instead of the F—A distances.[14] Experimental distances were taken from microwave spectroscopic studies and the location of H atoms was reasonably accurate, certainly within ±0.1 Å. They interpreted the H···A distances as the sum of contributions from H and A (eqn. (2) above). For the contribution from A, they looked at the electrostatic potential of A. Molecular electrostatic potential (MESP) is a one-electron scalar field, which is a physically observable property of molecules.[15–17] It plays a key role in intermolecular interactions. The MESP at a point **r**, due to nuclear charges $\{Z_A\}$ at $\{\mathbf{R}_A\}$ and electron density, $\rho(\mathbf{r})$ of the molecule under consideration, is given by:

$$V(\mathbf{r}) = \sum_{A} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}^3\mathbf{r}'$$

The first and second terms on the r.h.s. of this equation represent the bare nuclear and electronic potentials, respectively. The sign of $V(\mathbf{r})$ in any particular region depends on whether nuclear or electronic effects are dominant there. The minimum observed in the MESP symbolizes the site of electron localization in a molecule and acts as a probable proton acceptor. The location of this minimum, Gadre and Bhadane pointed out, could explain the radial and angular geometry in FH···A complexes. The distance from the electrostatic minimum to A is taken as the contribution from A, $R_E(A)$. For most cases, $R_E(A)$ was close to the van der Waals radius of A. Moreover, they noted that a plot of the distance between A and H, R_{AH} *versus* R_E was linear with a slope very close to 1 *i.e.* 1.04 (eqn. (2)). The intercept in this case turned out to be 0.47 Å, which was taken to be an estimate of van der Waals radius of H. This is much shorter than the van der Waals radius for H atom which is 1.2 Å according to Pauling[8] and Bondi[18] and 1.1 Å according to Scott Rowland and Taylor.[19] Gadre and Bhadane argued that FH···A complexes involve hydrogen bonding and hence it was not surprising that the value determined (0.47 Å) was less than the van der Waals radius of H.

Mandal and Arunan carried out a similar analysis of all DH···A complexes, where D = F, Cl, Br and CN.[20] They noted that the slope of R_{AH} *versus* $R_E(A)$ plots varied between 0.9 and 1.1. Hence, they plotted $R_{AH} - R_E(A)$ *versus* $R_E(A)$ and forced the slope to be 0. They defined the intercept of this plot as the hydrogen bond radius for HD. This led to hydrogen bond radii, R_H, of 0.55 ± 0.07, 0.74 ± 0.08, 0.80 ± 0.11 and 0.93 ± 0.07 Å, for HF, HCl, HBr and HCN, respectively. They noted that these radii had a linear correlation with the dipole moment of HD and the extrapolation to zero dipole moment gave an estimate of the true van der Waals radius of H as 1.0 ± 0.1 Å, in close agreement with earlier estimates. Later, this analysis was extended to H_2O and HCCH complexes and hydrogen bond radii were determined to be 0.78 ± 0.07 and 1.09 ± 0.05 Å for OH and CH groups, respectively.[21] The plot of R_H *versus* dipole moment is no longer linear as shown in Fig. 1. It extrapolates to the van der radius of H, 1.2 Å, at zero dipole moment. Similar data for NH and SH groups would be quite valuable as hydrogen bonding by these groups is very important in biological systems.[9,22] However, such analysis could not be carried out for SH and NH groups as microwave data on H_2S and NH_3 complexes were limited. Though several NH_3 complexes have been reported, almost all of them have NH_3 as H bond acceptor. Ammonia rarely acts as a proton donor in the gas phase and only two cases are known where it does. These are the $(NH_3)_2$ and C_6H_6–NH_3 complexes.[23,24] In condensed phase, though, there are plenty of examples of NH acting as a proton donor starting with the important DNA base pairs.[9] If available, such hydrogen bond radii could be used instead of the van der Waals radii of the heavy atoms in determining the presence of hydrogen bonds.

We note that Klein, using the atoms in molecules theory, has recently concluded that the radii of several atoms involved in hydrogen bonding, primarily involving OH groups, should be less than their van der Waals radii.[25] For instance, he concludes that hydrogen should be assigned a radius of 0.82 Å, very close to what Arunan and coworkers[21] have determined for the OH group from analyzing microwave data. However, as pointed out above, getting similar results from microwave data for NH and SH groups in the near future appears to be difficult (our laboratory is studying a series of H_2S complexes presently using a pulsed nozzle Fourier transform microwave spectrometer[21] to generate a larger database). Hence, it was decided to analyze crystal data for trends. Statistical analysis of crystallographic data is an established field in itself[2,9] and it has often been possible to identify interactions that were unexpected.[19,26–29] In particular, we refer to the paper by Taylor and Kennard[26] that established C–H···O hydrogen bonds in crystals. More recently, Novoa and coworkers have looked at hydrogen bonding involving ions[28,29] and discussed both charge assisted hydrogen bonding in O–H···O^- contacts and repulsive interactions between two OH^- groups. In this work, we limit ourselves to hydrogen bonding interactions in neutrals as the presence of ions certainly alters the nature of interactions. As X-ray crystallographic data are less reliable for locating hydrogen atoms, it was decided to analyze neutron diffraction data where available. Comparison of X-ray and neutron data reveals that it is possible to draw meaningful conclusions from the extensive X-ray structural data available.

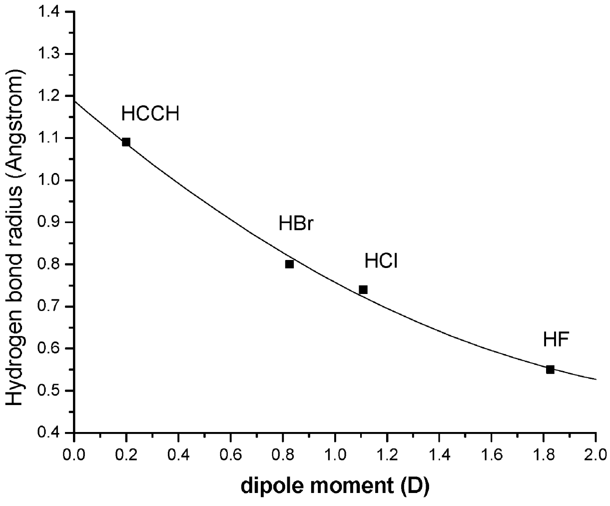

Fig. 1 Hydrogen bond radius for HF, HCl, HBr and HCCH determined from microwave spectroscopic data[20,21] and electrostatic potentials for various acceptors[14] plotted *vs.* the dipole moment.

Data analysis

The crystallographic data used in this survey were retrieved from the Cambridge Structural Database.[30] The radial and angular geometries of H bonding were investigated in detail for a series of H bond donors and acceptors. For donors, O–H, N–H, S–H and C–H groups were chosen. For acceptors, C=O, $-C_2O$, C≡N and pyridinic nitrogen were chosen. These acceptors were chosen, instead of simply specifying O or N atoms, as it eliminates the possibility of N or O being attached to H atoms, which can lead to secondary interactions. The R_E values for these acceptors were taken to be identical to the values for some model compounds. For C=O and C–O–C groups, CH_2O (formaldehyde) and $(CH_2)_2O$ (oxirane) were chosen as model compounds. For the C≡N group, HCN and CH_3CN were chosen as model compounds and the average value was used. For pyridine, R_E was directly calculated. The R_E's have been calculated for isolated gas phase molecules following the procedure described earlier.[14] However, for this work these R_E values were re-evaluated at a higher level with a larger basis set at HF and MP2/6-311++G(2d,2p) levels. Although the calculations were for isolated molecules, comparison of microwave data of the gas phase with the X-ray/neutron data of the condensed phase shows that the predicted trends are similar, *vide infra*. The calculated MP2(HF) R_E values for CH_2O, $(CH_2)_2O$, HCN, CH_3CN and pyridine are 1.32 (1.25) Å, 1.30 (1.24) Å, 1.38 (1.35) Å, 1.36 (1.33) Å and 1.30 (1.26) Å, respectively. The MP2 results were used for calculating the hydrogen bond radius. However, the difference between these two sets of R_E values are within the uncertainty reported later for hydrogen bond radii.

In order to resolve the ambiguities, if any, in CH···O hydrogen bonds, it was decided to look at a variety of donors with C–H groups. Searches were carried out with the H bond donor specified as C–H (which should include all types of CH groups), O=C–H (aldehydic), C≡C–H (acetylenic), CCl_3H, C–H_2C–H (methyl bonded to C), F_2C–H (difluoromethyl) and CH_2–H_2C–H (no electronegative substituent in the primary carbon). Fig. 2 defines the geometry as specified during the searches for two typical examples. The geometrical parameters determined were, (1) the hydrogen bond distance from H to the acceptor atom, B_1, (2) the hydrogen bond angle D–H···A, A_1, (3) the distance H–D, B_2 and (4) the dihedral angle formed by four atoms (D–H···A–C), T_1.

Search criteria for the structures were quite stringent. Only error free structures with R factors <4% were chosen for analysis using the Questv5 program of the Cambridge Crystal Structural Database suite of programs. Only intermolecular contacts were included. All structures containing the specified acceptor and the hydrogen bond donor with $B_1 \leq 3.5$ Å were harvested and the metric details mentioned above tabulated for analysis using the program Vista. The cutoff for the hydrogen bonding distance specified (3.5 Å) is significantly higher than the sum of the van der Waals radii of H (1.2 Å) and O (1.4 Å) or N (1.5 Å) atoms. A typical search routine used for retrieving data from the CSD is included in the supporting document.† Polar flattening of van der Waals radii *i.e.* angle dependent radii have been noted in the CSD analysis.[31–33] Legon and coworkers in their microwave studies, have described this phenomenon with respect to halogen atoms, using the term 'snub-nosed' atoms.[13] This effect has not been addressed in this work as our main emphasis is to establish that a hydrogen bond radius can be defined and it is consistent with the extensive data available in both gas phase and condensed phase structures.

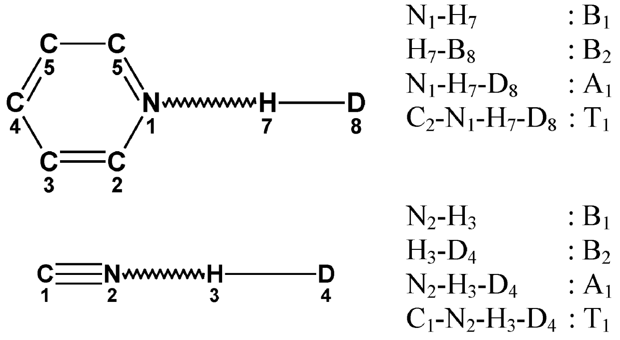

Fig. 2 Structural parameters extracted from the Cambridge Crystal Structure Database (CSD) defined for two typical cases. B_1 is the hydrogen bond distance and A_1 is the hydrogen bond angle.

Results and discussions

The search criteria used for arriving at the results presented here were based on several trial searches with different cut off distances to make sure that no relevant data were discarded. Various combinations of H bond donors and acceptors were trawled from the Cambridge Structural Database. Some of these searches were done using X-ray and neutron scattering data, independently. For many cases, the database had a comparatively insignificant number of hits for neutron scattering. However, in some cases, there were enough data to make a meaningful comparison. Fig. 3 shows the histogram of O···H distances found for C=O···H–O contacts using X-ray and

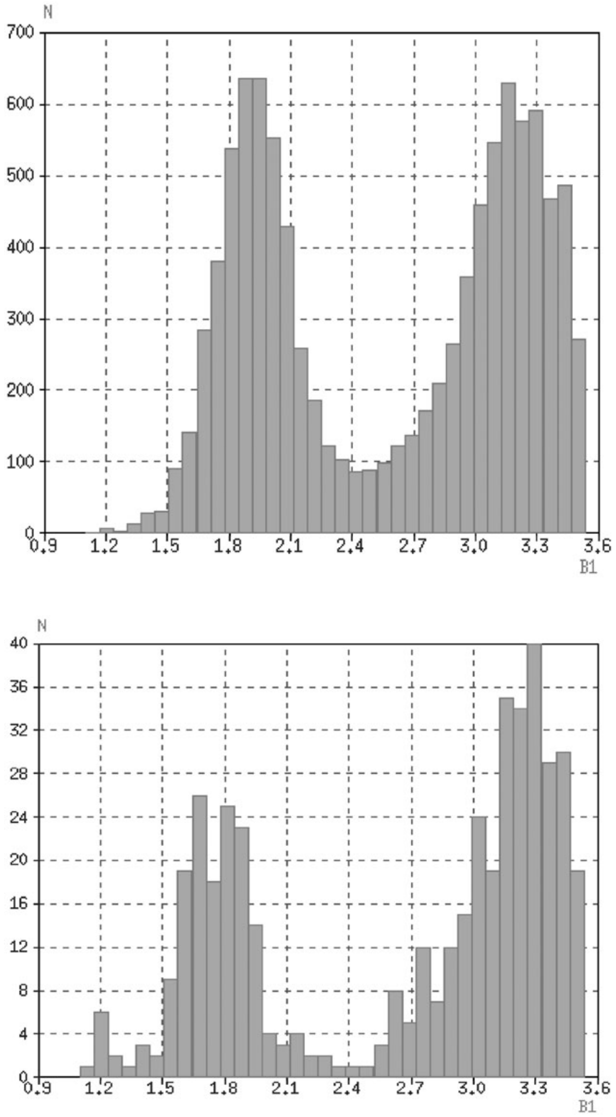

Fig. 3 The histogram of hydrogen bond distances for O–H···O=C contacts from CSD from X-ray diffraction (top) and neutron diffraction (bottom) results. In all histograms N is the number of contacts and $B1$ is the hydrogen bond distance in Å.

neutron scattering data. For X-ray scattering, the number of data points was 10 000 (as restricted by the analysis software for meaningful statistical analysis) and for neutron scattering it was only 459. The histograms from both data sets show a clear peak corresponding to hydrogen bonding interactions. The results presented in Fig. 3 convince us that conclusions drawn exclusively from X-ray structural data will be meaningful. The peak was observed at 1.9 Å for X-ray data and 1.8 Å for neutron data. In our earlier work,[20,21] this distance was assumed to be the sum of R_E(A) (distance from the bonding atom/center to the electrostatic minimum) for the H bond acceptor and R_H(DH) (H bond radius for DH). Similar histograms of H···O distances for C–H···O=C contacts are shown in Fig. 4, for various CH groups. For Cl_3CH, –C≡CH and O=C–H, a clear hydrogen bonding peak is observed. However, for H–CH_2–C and H–CH_2–CH_2 no peaks are observed. Moreover, the shortest contact distance observed is longer for H–CH_2–CH_2 than that for H–CH_2–C. A similar trend is observed for pyridinic N–HD contacts as given in the supporting information, Fig. S1.† For D=O and N, there is a clear hydrogen bonding peak. The shortest contact distance increases from D=C to D=CH_2–C to D=CH_2–CH_2 and there is no obvious hydrogen bond peak.

This behavior in hydrogen bond distances has been noted by Desiraju and Steiner in Fig. 2.11 of their book. However, they point out that the hydrogen bond angles have a distribution peaking at 180° for most C–H···O contacts (Fig. 2.18, ref. 2), though they are very broad. The histograms of this angle, after conical corrections, are shown in Fig. 5 for pyridinic(N)···HO and pyridinic(N)···H–CH_2–CH_2. For the OH contacts, the distribution of angles are plotted for the hydrogen bond peak (B_1 = 1.6–2.3 Å) and independently for the structures with $B_1 > 2.4$ Å. Not surprisingly, the histogram shows a sharp peak at 180° for the structures within the hydrogen bond peak. For larger distances, the histogram is flat and broad with a nominal peak at 60°. Hence, even for O–H···N contacts, if the H···N distance is longer than 2.4 Å (0.3 Å smaller than the sum of van der Waals radii of H and N atoms), a hydrogen bonding interaction may not be there. For pyridine···H–CH_2–CH_2 contacts, for the complete data presented (bond distances 2.6–3.5 Å), the histogram shows a broad distribution that still peaks at 180°, very similar to what is reported by Desiraju and Steiner. However, after looking at the difference in the angle distribution for O–H···N contacts at two different length scales, it was decided to look at the angle distribution for different ranges of H···N distances in C–H···N contacts. After a few trials, it was noted that the distribution of angles was strikingly different for H···N distances below 3.0 Å compared to the same for H···N distances between 3.0 Å and 3.5 Å. The similarity in the directionality for C–H···N and O–H···N contacts shown in Fig. 5 is quite revealing. It appears that the main reasons for not observing a hydrogen bond peak in the histograms (Figs. 4 and S1) for C–H···O/N distances could be the huge number of such contacts adding more noise in the distribution and the weakness of this interaction. Also, it appears that the radius for hydrogen bonded to C with no electronegative substituents, could be higher than the accepted van der Waals radius of H.

For the C≡CH and OH groups bonding to C=O, hydrogen bond peaks are observed at 2.36 Å and 1.85 Å, respectively. Subtraction of R_E(A), 1.32 Å, from these peaks (Figs. 3 and 4) gives their respective H bond radii as 1.04 Å and 0.53 Å, respectively. For comparison, microwave spectroscopic data of HCCH and H_2O complexes give these values as 1.09 Å and 0.78 Å, respectively.[21] The H bond radii determined for HCCH from gas phase data and CCH from X-ray data are very close. For the strongly bonding OH, the gas phase data give a radius that is 0.25 Å larger than that found from condensed phase. For C_2O as the acceptor, the hydrogen bond radius of OH is determined to be 0.68 Å, which is within 0.15 Å of the gas phase value. One unambiguous conclusion is that the OH group has a hydrogen bond radius that is 0.3–0.5 Å smaller than that of the acidic CH group.

The hydrogen bond radius determined for the various donor–acceptor combinations are summarized in Table 1. The error limits quoted (about 0.15 Å) are the half-widths of the hydrogen bond peaks from the histograms. For the CH donors, the peak width could not be determined (see Figs. 3, 4 and S1) and hence error limits are not quoted. Considering the weaker interaction involving CH bonds, the error limit should be at least 0.15 Å. In addition to this distribution, Table 1 shows how the hydrogen bond radii vary with acceptor. For OH, the values vary from 0.53 Å to 0.68 Å within the uncertainty found from the peak width. Similarly, for NH, the values are 0.83, 0.81, 0.77 and 0.67 Å, for CN, pyridine, C_2O and C=O as acceptors, respectively. For CH as proton donor, only for H–C≡C, H–C=O and $HCCl_3$, a clear hydrogen bond peak could be identified. For all of them, the hydrogen bond radii come out to be 1.1 Å or more with the exception of the $HCCl_3$ interaction with C=O which gives a value of 0.84 Å. It is interesting to note that the hydrogen bond radii for the donors show only a little variation with the acceptor. Bian[34] has recently reported an extensive theoretical analysis of 300 hydrogen bond pairs and concluded that the proton donor is more important than the acceptor in hydrogen bond formation. Data reported in Table 1 support this conclusion.

The histograms for the other CH donors C–CH_2–H and CH_2–CH_2–H did not give any peak and a hydrogen bond radius could not be assigned. A complete summary of the database analysis is given as supplementary information in two tables.† These tables give the data for OH, NH, SH, CH, H–C=O, H–C≡C, H–CCl_3, H–CH_2–C, H–CH_2–CH_2 and H–CF_2 as hydrogen bond donors. Table S1 has the peak values and hydrogen bond radii for each case and Table S2 gives the total number of hits and number of hits in the peak. For SH and H–CF_2 as donor, the number of hits was too small for a meaningful analysis. In most other cases, 10 000 entries were found.

The MESP minima used in Table 1 are for some model compounds. Obviously, the CSD data would have a wide range of substituents. In order to test the validity of the hydrogen bond radii quoted here, it was decided to calculate the MESP topological parameters,[15–17] including R_E values, for pyridine and C=O with different substituents. These calculations were done at the HF/6-31+G* level. The results are presented as supporting documents in Tables S3 and S4 for pyridine and C=O, respectively.† Also, the MESP values at these minima are given in these tables. A deeper minimum is expected to prompt an interacting acidic proton to approach closer. For substituents such as CH_3, CHO, NH_2, CH_3O, NH_2 and $(CH_3)_3$–N in *meta* and *para* positions, R_E varied little with values between 1.25 Å and 1.27 Å. The *ortho* substituted molecules were not included in the calculation because of the predominant neighbouring group effect on the MESP topography. In all these cases, the MESP minimum was located along the C_2 axis of pyridine to within 1°, justifying the 180° peak observed in Fig. 5. For NO_2 substituents in both *meta* positions with CN/COOH in *para* position, R_E is slightly larger at 1.30/1.31 Å. Similarly, for substituents such as H, CH_3, CH_3CH_2, CH_3O, F and NH_2, the R_E values for C=O varied from 1.20 Å to 1.26 Å. Of course, with C=O, there are two minima in the MESP which have slightly different values for unsymmetrically substituted compounds. Here again, substituents like NO_2 increase R_E to 1.36 Å and 1.41 Å. The data presented in these two tables suggest that the variation in R_E is generally within the uncertainty reported for the hydrogen bond radius in this work.

As this work was completed, we came across two papers that are very relevant. Firstly, a paper published by Wallwork in 1962 titled 'Hydrogen bond radii'.[35] Wallwork had written the heavy atom D—A distances as the sum of van der Waals radius

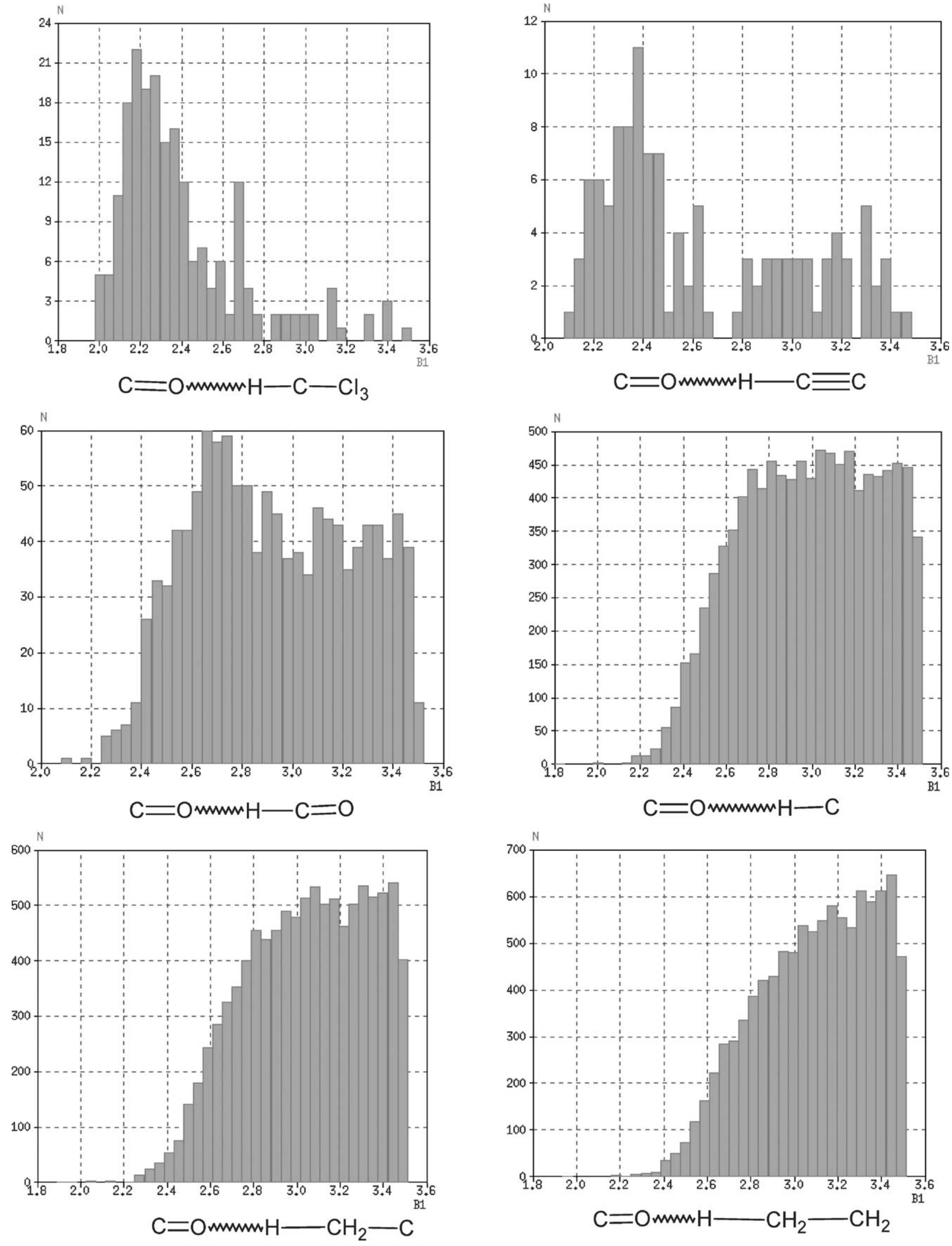

Fig. 4 Histograms of hydrogen bond distances for various CH donors with C=O as acceptor. Only for acidic CH groups, a hydrogen bond peak is present. The shortest contact distances increase as the CH group is defined more precisely from CH to C–CH_2–H to CH_2–CH_2–H. The latter has no electronegative substituent at the primary carbon.

of A and hydrogen bond radius of DH. Not surprisingly, H···A distances were not available at that time and hence not analyzed. This paper seems to have received significant attention earlier. However, recent books and papers do not mention this work. Very recently, Robinson and Gillespie[36] have reported the ligand radius of hydrogen determined by the geometry of nonmetal hydrides. These authors have estimated the radius of H atom bonded to D (D = B, C and N) by

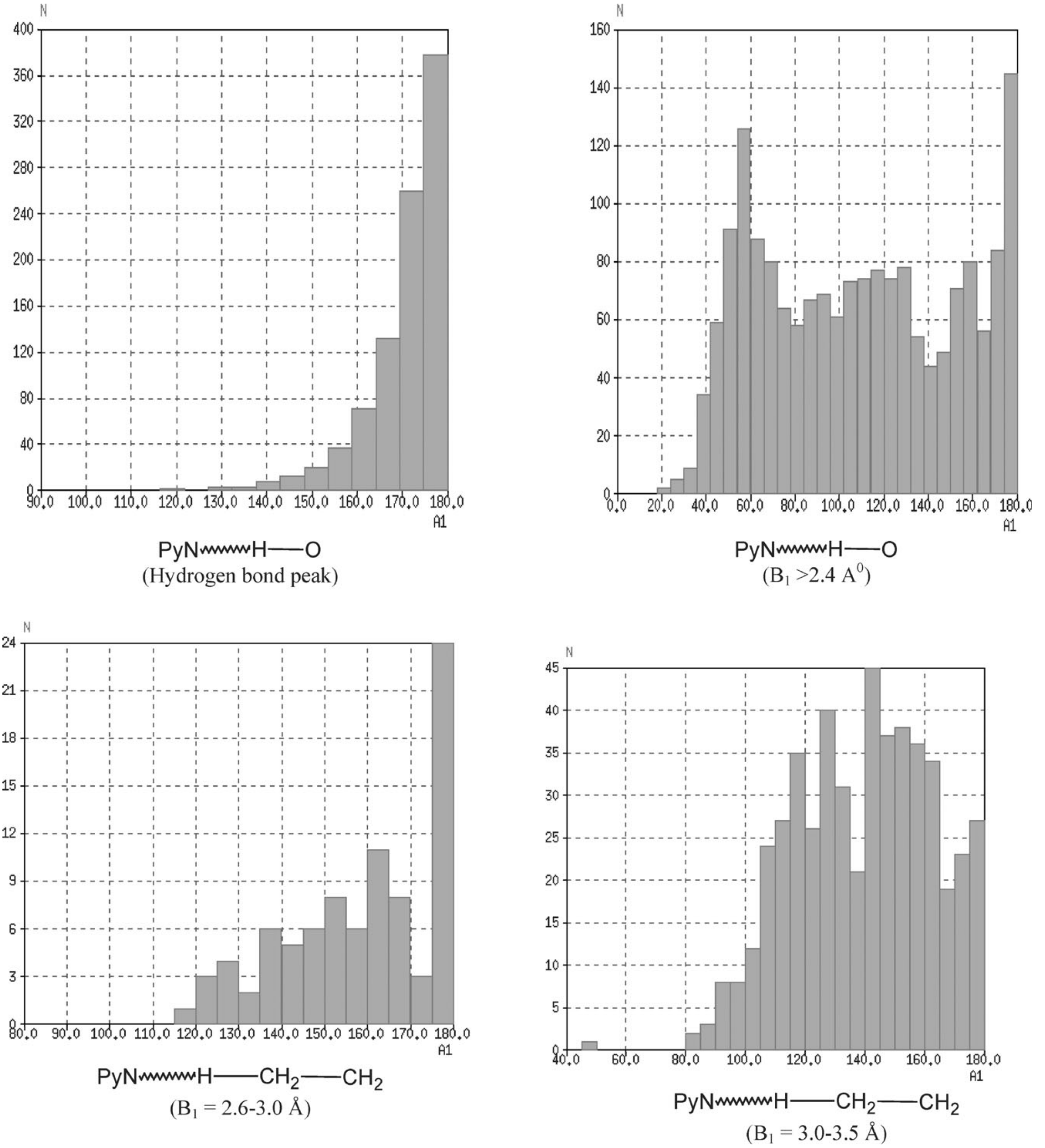

Fig. 5 Histograms of hydrogen bond angles for pyridinic(N)···H–O and for pyridinic(N)···H–CH_2–CH_2 contacts for different N–H distances as shown below the histograms. The histograms of distances are shown in the supporting information (Figure S1).†

Table 1 Hydrogen bond radius determined for OH, NH, O=C–H and C≡CH donor groups with C≡N, pyridine, C=O and C_2O as acceptors, from X-ray structural database analysis[a]

H–D	CN (1.37)	Pyridinic (1.30)	C_2O (1.30)	C=O (1.32)
H–O	0.61 ± 0.15	0.56 ± 0.15	0.68 ± 0.15	0.53 ± 0.15
H–N	0.83 ± 0.15	0.80 ± 0.15	0.75 ± 0.13	0.66 ± 0.15
H–C≡C	—	—	—	1.04
H–C=O	—	—	1.22	1.12
$HCCl_3$	—	1.07	1.02	0.84

[a] The value given in parenthesis in the column heading corresponds to R_E for the acceptor. See text for details. The hydrogen bond radius is determined by subtracting R_E from the peak distance of the bond distance histograms (as shown in Figs. 3, 4 and S1). For other CH donors such as C–CH_3 and CH_2CH_3, a peak was not found.

looking at H—H distances in DH_n. They argue that the hydrogens in DH_n have different sizes depending on the electronegativity of D and they closely pack with each other leading to the observed bond angle H–D–H. While, it is not clear if this view is generally accepted (are the hydrogens really in contact with each other?), we note that the estimated size of hydrogen bonded to C (0.94 Å) and N (0.82 Å) are very close to the hydrogen bond radius determined for CH and NH groups. For OH, the only data point they had was the H—H distance in H_2O and it again gives a radius of 0.76 Å, surprisingly close to the hydrogen bond radius reported in this work.

Conclusions

Previously, Arunan and coworkers have reported hydrogen bond radii for HF, HCl, HBr, HCN, H_2O and HCCH, by a systematic analysis of microwave spectroscopic data on hydrogen bonded complexes DH···A[20,21] and the electrostatic potential of A determined by Gadre and Bhadane.[14] In this present work it is shown that analysis of extensive condensed phase data obtained from X-ray and neutron diffraction corroborates their results. Particularly, for OH and C≡CH, the hydrogen bond radii determined from condensed phase data are in qualitative and quantitative agreement with gas phase data. In addition, for NH groups, the hydrogen bond radius has been determined. The hydrogen bond radii for OH, NH and CH groups are recommended as 0.60 ± 0.15 Å, 0.76 ± 0.15 Å and 1.10 ± 0.2 Å, respectively.

It is clear that the size of hydrogen increases as the electronegativity of D decreases. For acidic CH groups, the hydrogen bond radius comes out to be closer to the generally accepted van der Waals radius of the H atom. If the CH group is less acidic, as in hydrocarbons, the histograms of hydrogen bond distances do not show a peak. However, the hydrogen bond angle has unambiguous directionality very much like that of OH groups and the hydrogen bond radius for CH groups in hydrocarbons could be larger than 1.2 Å. For OH···N contacts, systems with H···N distances longer than 2.4 Å may not have hydrogen bonding, though this distance is less than the sum of the van der Waals radii of H and N atoms (2.7 Å). One final conclusion worth re-emphasizing is that the sum of van der Waals radii of atoms involved could be very misleading as a guideline for confirming or ruling out the presence of hydrogen bonds.

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