Harwell's *TAILS* computer program (Rouse, 1977) was used to refine a scale factor and the two isotropic temperature factors B_{Cu} and B_{Br}. The scattering lengths $b_{Cu} = 0.76 \times 10^{-12}$ cm and $b_{Br} = 0.679 \times 10^{-12}$ cm used for the calculated intensities were from Bacon (1972). The observed and calculated intensities are given in Table 1.

The R factor $= \sum (I_O - I_C)/\sum I_O$ was found to be 0.5%, which shows a very good agreement between the observed intensities I_O and the calculated intensities I_C.

The experimental results obtained from the above refinement were: $B_{Cu} = 2.85 \pm 0.33$, $B_{Br} = 2.71 \pm 0.33$ Å^2, $R = 0.005$. The Debye temperature obtained was $\theta = 131 \pm 8$ K, corresponding to the average $\bar{B} = 2.77 \pm 0.33$ Å^2. This value is in agreement with a recent value of $\bar{B} = 2.54$ derived from single-crystal neutron diffraction measurements (Harada, Suzuki & Hoshino, 1976).

In the above experiments we have not considered the possible effect of anharmonicity on the B values, which could modify them slightly. However, it would be interesting to find these parameters at low temperatures, such as 4.2 K, where the TDS and anharmonic corrections could become very small.

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The van der Waals Criterion for Hydrogen Bonding

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Existing neutron diffraction data for hydrogen-bonded solids have been studied in the light of the van der Waals criterion for hydrogen bonding. It was found that for the formation of A—H$\cdots B$ bonds the distance $A \cdots B$ should be less than the sum of the A—H covalent bond distance, the van der Waals radius of H and that of B. It has also been shown that with decrease in $A \cdots B$ distance, the A—H bond extends in a quantitative manner irrespective of what atoms A and B are. Particularly, for A—H$\cdots A$ bonds when the overlap of the van der Waals radii of two A atoms exceeds a certain high value, the A—H bond is extended so much that the H atom is placed at the midpoint between A and A resulting in a symmetrical hydrogen bond.

Nomenclature

$D(A-B)$ Observed distance between A and B in $A-H\cdots B$.

$D(A-H)$ Observed covalent bond distance of $A-H$ in $A-H\cdots B$.

$D(H-B)$ Observed distance between H and B in $A-H\cdots B$.

$R(A-H)$ Normal covalent bond distance of $A-H$ without hydrogen bonding (canonical value).

$R(A)$ Covalent radius of A.

$W(A), W(B), \ldots$ van der Waals radius of A, B etc.

$\delta R(AB)$ or $\delta R(AB)'$ Decrease of distance between A and B, where $\delta R(AB) = W(A) + W(B) - D(A-B)$, and $\delta R(AB)' = R(A-H) + W(H) + W(B) - D(A-B)$.

$\delta R(HB)$ Decrease of distance between H and B from the sum of the van der Waals radii of the atoms i.e. $\delta R(HB) = W(H) + W(B) - D(H-B)$.

$\delta R(A H)$ Increase of observed covalent bond distance from its canonical value, i.e. $\delta R(A H) = D(A-H) - R(A-H)$.

Introduction

The present paper describes our effort to find the functional relations that might exist among the relative positions of atoms A, H and B forming a linear hydrogen bond, $A-H\cdots B$, irrespective of what the atoms A and B are. It is thought that any well established empirical relation will be very useful not only to the crystallographers for comparing and contrasting their results, but also to those who are engaged in theoretical understanding of the nature of hydrogen bonding.

Relative positions of A, H and B in an $A-H\cdots B$ situation

(i) In the absence of hydrogen bonding, the distance between $O\cdots O$ in an $O-H\cdots O$ bond must be more than or equal to the sum of the $O-H$ covalent bond distance and the van der Waals radii of H and O (Speakman, 1972).

(ii) Hamilton & Ibers (1968) have also shown that the distance from H to B, $D(H-B)$, in $A-H\cdots B$ is considerably less than the sum of the van der Waals radii of H and B.

(iii) There is a definite correlation between $O\cdots O$ distance, $D(O-O)$, and the $O-H$ covalent bond distance, $D(O-H)$ (Nakamoto, Margoshes, and Rundle, 1955; Welsh, 1957; Pimentel & McClellan, 1960, p. 259, Fig. 9-1), and also between $D(O-H)$ and the $H\cdots O$ distance, $D(H-O)$ (Olovsson & Jönsson, 1976).

(iv) A straightforward attempt has been made to predict $D(A-H)$ vs $D(A-B)$ plots for any $A-H\cdots B$ hydrogen bond, where A or B is not oxygen, by the following ingenious computational method (Pimentel & McClellan, 1960):

$D(A-B)$ is first converted to $D(O-O)_{eq}$ by

$$D(O-O)_{eq} = D(A-B) + 2W(O) - W(A) - W(B), \quad (1)$$

where $W(A)$ is the van der Waals radius of A, etc. This $D(O-O)_{eq}$ is used to obtain $D(O-H)_{eq}$ from the $D(O-O)$ vs $D(O-H)$ plot. Finally, the predicted $D(A-H)$ is obtained by

$$D(A-H) = D(O-H)_{eq} + R(A) - R(O), \quad (2)$$

where $R(A)$ is the covalent radius of A, etc.

The predicted values of $D(A-H)$ have been within $\pm 0 \cdot 03$ Å of the experimental values. Different predicted plots have shown that a decrease of $D(A-B)$ is always associated with an increase of $D(A-H)$. On this basis we write:

$$D(H-B) = W(H) + W(B) - \delta R(HB) \quad (3)$$

and

$$D(A-B) = R(A-H) + W(H) + W(B) - \delta R(HB) + \delta R(A H) \quad (4)$$

or

$$D(A-B) = R(A-H) + W(H) + W(B) - \delta R(AB)', \quad (5)$$

where $\delta R(AB)' = \delta R(HB) - \delta R(A H)$.

Here δR represents the difference between canonical and observed values.

From (3) and (5) we have:

$$\delta R(HB) = W(H) + W(B) - D(H-B) \quad (6)$$

$$\delta R(AB)' = R(A-H) + W(H) + W(B) - D(A-B). \quad (7)$$

According to this representation, as $W(H)$ and $W(B)$ increasingly interpenetrate [i.e. $\delta R(HB)$ increases], the $A-H$ covalent bond distance increases accordingly [i.e. $\delta R(A H)$ increases]. This can very well imply that for a particular type of $A-H\cdots B$ bond (i.e. A and B are unaltered) $\delta R(HB)$ and $\delta R(A H)$, and for that matter, $\delta R(HB)$ and $\delta R(AB)'$ are interrelated. But, can we push this implication still further by suggesting that for any combination of A and B (such as $O-H\cdots O$, $O-H\cdots N$, $O-H\cdots F$ etc., or $N-H\cdots O$, $N-H\cdots N$, $N-H\cdots F$ etc., or $F-H\cdots F$), $\delta R(HB)$ is uniquely related to $\delta R(AB)'$? Certainly, it is worth while to find out whether this relation can be established on empirical grounds.

Calculation and results

In understanding hydrogen bonding in crystals, the location of relevant protons is crucial. For this, neutron

diffraction is the only method of general reliability. Our study is therefore restricted to results thus derived.

Olovsson & Jönsson (1976) have tabulated a large number of neutron diffraction data for different $A—H\cdots B$ hydrogen bonds in solids, of which bond distance data have standard deviations of less than 0·02 Å. We have used these values for both asymmetric and symmetric bonds with the $A—H\cdots B$ angle more than 160°. A few data have been added for $O—H\cdots F$ (Abrahams, 1962; Abrahams & Prince, 1962) and symmetric $F—H—F$ (McGaw & Ibers, 1963) bonds with standard deviations of less than 0·02 Å in bond distances.

The van der Waals radii of different atoms were first estimated by Pauling (1939) and later revised by Bondi (1964). In the present work Bondi's mean values for different atoms, except H, have been used: $W(N) = 1·55$, $W(O) = 1·52$, $W(F) = 1·47$, $W(Cl) = 1·75$ Å. The most favoured value of $W(H)$, 1·00 Å, is used in our calculations. [Bondi's mean value for $W(H)$ is 1·20 Å. It will be seen, that whatever value for $W(H)$ is chosen, it does not affect the important aspects of this work.] The canonical normal covalent bond distances are taken from *International Tables for X-ray Crystallography* (1968): $R(O—H) = 0·96$, $R(N—H) = 1·01$ and $R(F—H) = 0·92$ Å.

Using equations (7) and (6), $\delta R(AB)'$ and $\delta R(HB)$ for these neutron diffraction data are calculated. The plot of $\delta R(AB)'$ *vs* $\delta R(HB)$ is shown in Fig. 1. It is
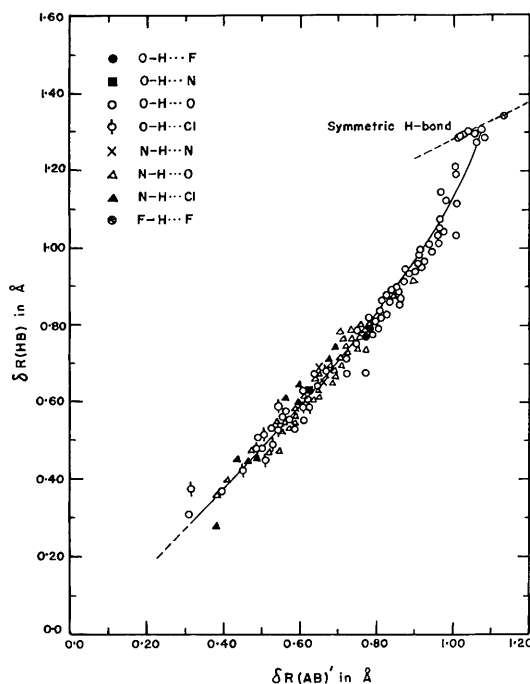
observed that $\delta R(AB)'$ and $\delta R(HB)$ values with crystal data of several bond types fall excellently on a smooth curve.

Hamilton & Ibers's (1968, p. 15) operational criterion for the existence of a hydrogen bond, that the 'two electronegative atoms are closer together than the sum of the van der Waals radii' is largely followed. Including the fact that as the atoms A and B become closer and closer, $D(A—H)$ is consequently extended, we formulate the following:

$$\delta R(AH) = D(A—H) - R(A—H) \qquad (8)$$

and

$$\delta R(AB) = W(A) + W(B) - D(A—B). \qquad (9)$$

$\delta R(AB)$ and $\delta R(AH)$ are calculated from the same data and the plot of $\delta R(AB)$ *vs* $\delta R(AH)$ is shown in Fig. 2. In Fig. 2 the solid curve, drawn according to the best least-squares fit, follows the relation:

$$Y = 0·0042 + 0·0799X - 0·7159X^2 + 1·7595\,X^3, \qquad (10)$$

where $Y = \delta R(AH)$ and $X = \delta R(AB)$.

The prediction of $\delta R(AH)$ from $\delta R(AB)$, has a standard deviation of 0·021 Å. Therefore, $D(A—H)$ values (and thus the position of the H atom) can be obtained by the following relation:

$$D(A—H) = R(A—H) + \delta R(AH), \qquad (11)$$

where $\delta R(AH)$ is calculated by equation (10).

Fig. 1. Plot of $\delta R(HB)$ *vs* $\delta R(AB)'$. The solid curve corresponds to: $Y = -0·3335 + 2·7790X - 3·0920X^2 + 1·7800X^3$, s.d. $= 0·021$ Å, where $Y = \delta R(HB)$ and $X = \delta R(AB)'$.

Discussion

We should observe in Fig. 1 that there is a complete absence of data between 0·00 and 0·31 Å on both axes and very few up to 0·45 Å. There should be a huge number of crystals whose data for $A—H\cdots B$ could fill these vacant spaces; but crystallographers do not regard these as genuine hydrogen bonds which apparently agree with Hamilton & Ibers's (1968) operational criterion [since $R(A—H) + W(H) - W(A) \simeq 0·44$ Å]; and so no geometrical details are published about them. Hamilton & Ibers's operational criterion is rather arbitrary. For weak hydrogen bonds which are based on knowledge of the hydrogen atom position Hamilton & Ibers had to suggest that 'distance from the hydrogen atom to the more weakly bound atom be considerably less than the sum of the van der Waals radii of hydrogen and the heavy atom'.

It should be noted that the curve in Fig. 1 has been drawn following Speakman's suggestion (Speakman, 1972) and it can certainly cover hydrogen bonds from extremely weak to very strong ones until symmetric bonds appear.
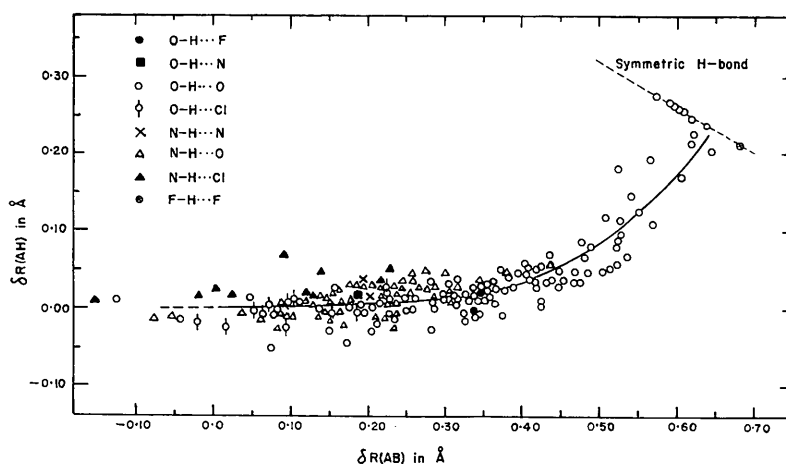
Fig. 2. Plot of $\delta R(AH)$ vs $\delta R(AB)$. The solid curve is drawn according to equation (10).

However, the formulation shown in (10) and Fig. 2 is not inoperative in cases of weak hydrogen bonding, the only difference from Fig. 1 is that the data points appear on the negative side of the $\delta R(AB)$ axis. A good advantage of (10) is that one does not need to use the van der Waals radius of the H atom, the assignments of a canonical value to which differ widely (1·00–1·20 Å).

From Fig. 2 it becomes evident that (i) while $W(A)$ and $W(B)$ interpenetrate, increasing the value of $\delta R(AB)$ from 0·0 to 0·55 Å, the extension of the A—H covalent bond distance is very small indeed; (ii) when $\delta R(AB)$ is greater than 0·55 Å, the H nucleus falls within the span of $W(B)$ and the extension of the covalent bond distance rapidly increases; (iii) on continuation of interpenetration of $W(A)$ and $W(B)$ further, a point is reached when $\delta R(AB)$ is nearly equal to 0·65 Å and a situation is arrived at where $\delta R(AH)$ is so high that $D(A—H) = \frac{1}{2}D(A—B)$, giving rise to a symmetrical hydrogen bond if A and B are of the same type. Further interpenetration of $W(A)$ and $W(B)$ does not alter the symmetrical position of the H atom between A and B; presumably the centroid of the electron density is now permanently at the midpoint of A and B.

Remarks

A considerable spread of data points is observed in Fig. 1. This scatter was also observed in a $D(O—H)$ vs $D(O—O)$ plot by Olovsson & Jönsson (1976, p. 411, Fig. 8–12). These spreads cannot be explained by experimental errors alone. Certainly, widely differing environments of A—H$\cdots B$ must have strong influences. We have assumed 'the invariance of the van der Waals radius of an atom even under the most drastic environmental changes, *i.e.* irrespective of its chemical combination and of its nearest nonbonded neighbours ....' (Bondi, 1964). In fact, each of the crystal data could be subjected to calculation with the most suitable value of the van der Waals radius of the atom involved, considering the environments where these exist.

Thus, we are led to conclude that the observed deviation of the H atom from the position obtained by (10) should be discussed in each case in the light of the detailed bonding situation in the solid crystals and it should be worth while to assign relative causes leading to such deviations.

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