Table referenced as "Wallwork H [hydrogen] bond lengths (Dia.)"

Contributors

Fuller, Watson, 1935-

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The values of intermolecular hydrogen-bond distances, mainly in organic crystals, have been collected in order to investigate the possibility of expressing these distances as a simple function of values characteristic of the two groups participating in the formation of the hydrogen bond. This compilation represents a fairly extensive coverage of the literature up to 1960, but the individual values and references are not given in view of the previous publication of similar lists (Donohue, 1952; Fuller, 1959; Pimentel & McClellan, 1960). The distances $Y \cdots Z$ have been classified according to the type of donor group Y–H and acceptor group Z in the bond Y–H $\cdots Z$. Within each class the distances have been averaged and the standard deviation has been calculated. The data so obtained are shown in the first two lines of figures in each portion of Table 1.

Examination of the average values shows that, for a given donor group, the hydrogen-bond distances follow roughly the change in the van der Waals radii of the accep[redacted] atom in Z [redacted] given acceptor group the hydrogen-bond distances decrease with increasing electronegativity of the atom attached to H in the donor group Y–H. It is found, in fact, that the decrease from the expected van der Waals distance between H and Z brought about by hydrogen-bond formation is roughly proportional to the difference in electronegativity between the hydrogen atom and the atom to which it is attached in the donor group Y–H.

These observed trends suggest that it might be possible to express hydrogen bond distances as the sum of two hydrogen bond radii, one a constant for a given donor (Y–H) group and one a constant for a given acceptor (Z) group. They also suggest that the best assumption in the apportionment of each total distance among the two groups might be obtained by taking the hydrogen-bond radius for one acceptor atom as equal to its van der Waals radius. In view of the preponderance of hydrogen-bond distances with oxygen atoms as acceptors, it was decided to take the hydrogen-bond acceptor radius of an oxygen atom as being equal to 1·40 Å. Starting from this basis, it was found to be possible to calculate a set of hydrogen-bond radii which [redacted] produce [redacted] ances. These hydrogen-bond radii are given in Table 2 and the expected hydrogen-bond distances calculated from them are shown on the third line of each section in Table 1.

Although only the hydrogen-bond acceptor radius

Table 1. *Observed and calculated average hydrogen bond lengths*

Data in each entry in the table are:

1st line — average observed hydrogen bond length ($Y \cdots Z$, in Å)
2nd line — standard deviation and, in parentheses, the number of values averaged
3rd line — calculated hydrogen bond length, from the radii of Table 2

(* indicates data taken from Fuller, 1959)

Donor group Y–H	Acceptor group Z (in the hydrogen bond Y–H $\cdots Z$)									
	Br^-	Cl^-	NH_3	N	OH_2	O	O^-	NH_3^+	N^-	F^-
NH_3			3·17 0·12(12) (3·14)	3·07 0·11(25) (3·06)	3·06 0·16(17) (3·03)	2·93 0·11(69) (2·95)	2·98 0·15(14) (2·98)	less-well-established averages		
NH_3^+	3·39* 0·06(11) (3·39)	3·19* 0·07(34) (3·20)	3·00 0·08(15) (3·00)	2·92 0·05(4) (2·92)	2·94 0·18(12) (2·89)	2·86 0·08(7) (2·81)	2·83 0·10(74) (2·84)	3·06 — (1) (3·09)	2·93 0·05(4) (2·93)	2·73 0·09(4) (2·76)
OH_2	3·29 0·10(6) (3·28)	3·12 0·16(15) (3·09)	2·82 0·08(8) (2·89)	2·78 0·10(10) (2·81)	2·76 0·10(74) (2·78)	2·72 0·04(57) (2·70)	2·75 0·13(20) (2·73)	2·99 0·03(2) (2·98)		2·70 0·13(2) (2·65)