Hydrogen-Bond Radii

By S. C. Wallwork

Department of Chemistry, University of Nottingham, England

A table of classified average intermolecular hydrogen-bond distances (Y–H $\cdots Z$) is presented. It is shown that these average distances can be represented, to a sufficient degree of accuracy, by the sums of two hydrogen-bond radii, one a constant for each donor group Y–H and one a constant (approximately equal to the van der Waals radius) for each acceptor group Z.

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 acceptors Z, except where the electronegative atom in Z is directly attached to hydrogen. For a 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, when added appropriately, reproduce well the observed average hydrogen-bond distances. 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)

Acceptor group Z (in the hydrogen bond Y–H $\cdots Z$)

Donor group Y–H	Br⁻	Cl⁻	NH$_n$	N	OH$_n$	O	O⁻	NH$_n^+$	N⁻	F⁻
NH$_n$			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$_n^+$	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$_n$	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)

Table 2. *Hydrogen-bond radii*

(Less-well-established values in parentheses)

Donor groups	(Å)	Acceptor groups	(Å)		(Å)		(Å)
NH_n	1·55	N^-	(1·52)	O^-	1·43	F^-	(1·35)
NH_n^+	1·41	N	1·51	O	1·40	Cl^-	1·79
OH_n	1·30	NH_n	1·59	OH_n	1·48	Br^-	1·98
		NH_n^+	(1·68)				

of oxygen was assumed to be the same as the van der Waals radius, it may be seen that the other acceptor radii for atoms not attached to hydrogen follow the van der Waals radii very closely. This fact may be used to predict the acceptor radii for other atoms, e.g. sulphur might be expected to have a value of about 1·85 Å, or possibly less in view of shorter van der Waals radii for sulphur adopted by some authors. Eighteen $NH_n \cdots S$ contacts which might be hydrogen bonds have been found in the literature. They range in length from 3·23 to 3·51 Å and have a mean value of 3·40 Å, which is the distance expected for hydrogen bonds of this type if the acceptor radius for sulphur is 1·85 Å. Five of these distances—3·26 (Penfold, 1953), 3·42 (Nardelli, Braibanti & Fava, 1957), 3·23 (Cavalca, Nardelli & Branchi, 1960), 3·44 and 3·50 (Dvoryankin & Vainshtein, 1960)—were described as hydrogen bonds by the authors who reported them. A distance $OH \cdots S$ of 3·246 Å for which a hydrogen bond is suggested (Nardelli, Fava & Giraldi, 1962) is also consistent with an acceptor radius for sulphur of approximately 1·85 Å.

The short hydrogen bonds of lengths about 2·6 Å in carboxylic acids, although not included in Table 1, may nevertheless be brought into the suggested scheme if they are imagined as being formed from a OH_n^+ donor, with a not unreasonable hydrogen bond radius of about 1·2 Å, and a O^- acceptor.

The chief limitation in the prediction of hydrogen-bond lengths by the addition of hydrogen-bond radii is the rather large variation in length found for any one type of hydrogen bond. One reason for this variation is the fact that each crystal structure must be the result of a compromise between a number of different attractive and repulsive intermolecular forces which may be of similar magnitude, and the way in which the compromise is reached affects the observed hydrogen-bond lengths. Another reason, which the present analysis of the data brings out clearly, is that the lengths of hydrogen bonds are very sensitive to the electron distribution in the Y–H donor groups. It is hoped that the establishment of typical average hydrogen-bond distances may serve as a basis for more detailed discussion of individual distances in terms of the electron distributions within the donor groups.

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The Crystal Structure of Shellolic Bromolactone Hydrate

BY E. J. GABE*

Viriamu Jones Laboratory, University College, Cardiff, Wales, and Division of Pure Physics, National Research Council, Ottawa, Canada

Shellolic bromolactone hydrate is orthorhombic ($P2_12_12_1$, $a = 7·07$, $b = 14·80$, $c = 15·56$ Å and $Z = 4$). The structure was determined by the application of the 'heavy atom' technique to the three-dimensional data and refined by differential syntheses. The structure found is in complete agreement with that proposed for shellolic acid by Yates & Field on chemical grounds, and confirms that the carbon skeleton is that of cedrene. The six-membered ring is in the chair form and the Br atom is *trans* to O_3, the oxygen atom of the γ-lactone ring.

Introduction

Shellolic acid $C_{15}H_{17}O_2$ is a component of shellac, a resin originating from the lac insect (Tschirch &

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* National Research Council Postdoctorate Fellow.

Stock, 1936). Earlier work on the acid (Nagel & Mertens, 1937, 1939) failed to establish the skeleton to which the functional groups are attached, and the present analysis was undertaken to assist recent chemical work. It was known at the outset that the