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The Variation in Carbon-Halogen Bond Length with the Environment

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The data on carbon-halogen bond lengths which have been obtained in recent years are summarized. It has been found that the interatomic distances corresponding to carbon-halogen bonds show a linear dependence on the number of adjacent atoms or bonds. Simple equations for these bond lengths are given to make it possible to estimate different carbon-halogen bond lengths empirically. It has been shown that this variation can be adequately explained on the basis of the hybridization effect. New values for the radii of the hybrid orbitals of carbon have been assigned and used to calculate the bond lengths in a variety of compounds. The agreement between calculated and experimental values is good.

As a result of the development of microwave spectroscopy for the study of the structure of the molecules, a large amount of information about interatomic distances in molecules has been accumulated. The accuracy of bond lengths determined experimentally depends upon the nature of the method used. The spectroscopic values for simple molecules are accurate to within ±0.001 Å, while those for polyatomic molecules are somewhat less reliable. This accuracy has made it possible to derive relationships between bond lengths and various other bond properties. The dependence of the carbon-carbon and carbon-hydrogen bond lengths on the environment has been studied by many workers.[1-6] An analysis of these data has led to an empirical relationship for the C–C, C=C, C≡C and C–H bond lengths, which increase linearly with the increase in the number of adjacent bonds or atoms. This paper will deal with the carbon-chlorine, carbon-bromine and carbon-iodine bond lengths in simple polyatomic molecules. Recent experimental values for carbon-halogen bond lengths in polyatomic molecules seem to depend linearly on the environment. Simple empirical equations have been given to estimate the different carbon-halogen bond lengths. Many attempts[7-14] have been made to explain the variation in carbon-carbon and carbon-hydrogen bond lengths with the environment in terms of various descriptions of carbon atoms and their environment. It will be shown in this paper that the variation in carbon-halogen bond lengths can be explained on the basis of the hybridization effect. New values for the radii of the hybrid orbitals of carbon have been assigned, and these values have been used to calculate the bond lengths in a variety of compounds. It has been found that the calculated and the experimental values are in agreement.

A Summary of Carbon-Halogen Bond Lengths in Polyatomic Molecules.—The values of the bond lengths, the molecules from which they have been obtained, and the method by which they are determined are given in Table I. The quoted bond-length values may be supposed to be the best values available at the present time. Most of the

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values have been obtained from microwave spectroscopic methods; they have been reported to be accurate to about ±0.005 Å. Some values not available from microwave spectroscopic methods involve larger experimental errors because they are not independent of some assumptions. Moreover, a small amount of uncertainity is also involved as a result of zero point vibrations, as the data pertain to the ground vibrational state and are not equilibrium bond lengths. A few values obtained from X-ray and electron diffraction data are accurate to only ±0.04 Å and require rectification by means of microwave spectroscopic methods.

It may be seen that the data of carbon-chlorine, carbon-bromine and carbon-iodine bond lengths confirm the earlier conclusions[4-6] that the bond lengths increase linearly with the increase in the number of adjacent bonds or atoms. This may easily be seen in Fig. 1, where the bond lengths are plotted against the number of adjacent bonds. In the figure all the bonds are equally well represented by lines with the slope of $0.070\,n$; i. e., all the lines are parallel. Most of the values for bond lengths lie within ±0.015 Å of the straight lines give by:

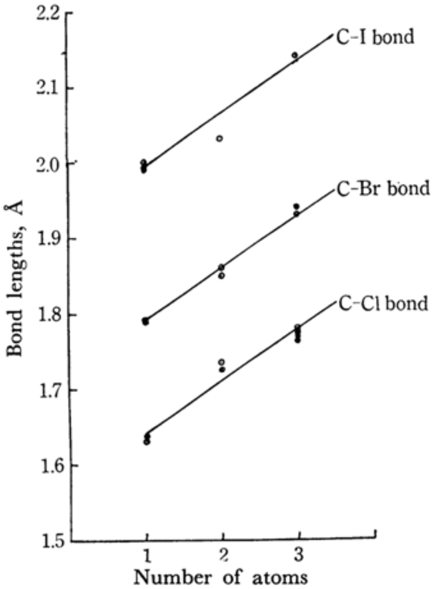

Fig. 1. A graph of carbon-chlorine, carbon-bromine and carbon-iodine bond lengths plotted against the number of adjacent atoms (or bonds).

$$r(\text{C–Cl}) = 1.575 + 0.070\,n \qquad (1)$$

$$r(\text{C–Br}) = 1.725 + 0.070\,n \qquad (2)$$

$$r(\text{C–I}) = 1.925 + 0.070\,n \qquad (3)$$

where $n=1$, 2 or 3.

Theory and Calculations

The properties of a bond depend upon the average number of electrons in it, their distribution among the molecular orbitals, and the concentration of the orbitals (as given by hybridization). Bond lengths are affected by changes in the hybridization of the orbitals forming the bond. Walsh[15] has pointed out that an increase in the s-character of the hybridization of carbon while passing from sp^3 to sp hybridization produces a stronger and shorter bond. Somayajulu[16] has shown that the strengths of the hybrid orbitals of carbon are in the order $sp > sp^2 > sp^3$; because stronger bonds are shorter, it is obvious that the radii of these orbitals will be in the order $sp^3 > sp^2 > sp$. Considering the CC "single bonds" it is evident from the accumulated structural data[6] that the best values for the lengths of the $\geqslant$C–C$\leqslant$, >C–C< and ≡C–C≡ bonds are 1.534±0.005 Å, 1.472±0.005 Å and 1.378±0.005 Å respectively. If it is assumed that the $\geqslant$C–C$\leqslant$, >C–C< and ≡C–C≡ bonds represent the tetrahedral (sp^3-sp^3) trigonal, (sp^2-sp^2) and digonal (sp-sp) bonds, we obtain for the radii of tetrahedral, trigonal and digonal carbon atoms the values of 0.767 Å, 0.736 Å and 0.689 Å respectively, which are very near to Lide's values (Ref. 14).

To account for the variation in carbon-chlorine, carbon-bromine and carbon-iodine bond lengths with the number of adjacent atoms or bonds, we have taken the covalent radii of chlorine, bromine and iodine to be 0.99, 1.14 and 1.33 Å respectively.[17] The values calculated for these bond lengths by the addition of the radii of hybrid orbitals of carbon and covalent radii of halogens and by applying of Schomaker-Stevensen correction[18] are given in Table I. Here the Schomaker-Stevensen coefficient has been given the value of 0.08.[17] It may be observed that in many instances the Schomaker-Stevensen correction gives a good agreement with the experimental values; in other instances, the additivity rule without this correction gives a better agreement. For example, the experimental values in ≡C–Cl, >C–Br and ≡C–Br bands are fairly well reproduced by taking into account the Schomaker Stevensen correction, while in the case of $\geqslant$C–Cl, >C–Cl and $\geqslant$C–Br bonds, the sum of the orbital radii gives a better agreement with the experimental values. It is not surprising that there are many exceptios to the Schomaker-Stevensen rule. In the case of carbon-iodine bonds, the Schomaker-Stevensen term becomes zero because the carbon and iodine have the same electronegativity value.

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TABLE I CARBON-CHLORINE, CARBON-BROMINE AND CARBON-IODINE BOND LENGTHS

Bond type	Sum of the orbital radii r_A+r_B Å	$r_A+r_B-0.08\|x_A-x_B\|$ Å	Obsd. length Å	Name of the substance	Formula	Method	Reference
⩾C–Cl	1.757	1.717	1.781	Methyl chloride	CH_3Cl	MS	20
			1.78	Butyl chloride	$(CH_3)_3CCl$	MS	21, 22
			1.778	Ethyl chloride	C_2H_5Cl	MS	23
			1.772	Methylene chloride	CH_2Cl_2	MS	24
			1.770	Trichloroacetonitrile	CCl_3CN	MS	22, 25
			1.767	Chloroform	$CHCl_3$	MS	26, 27
>C–Cl	1.726	1.686	1.726	Vinyl chloride	C_2H_3Cl	MS	28
			1.734	1,1-Dichlorocyclopropane	$C_3H_4Cl_2$	MS	29
≡C–Cl	1.679	1.639	1.630	Chlorocyanide	ClCN	MS	31
			1.637	Methylchloroacetylene	CH_3CCCl	MS	30
⩾C–Br	1.907	1.883	1.940	Ethyl bromide	C_2H_5Br	MS	32
			1.94	Butyl bromide	$(CH_3)_3CBr$	MS	22
			1.939	Methyl bromide	CH_3Br	MS	20, 33, 34, 35
			1.930	Bromoform	$CHBr_3$	MS	36, 37
>C–Br	1.876	1.852	1.85	Vinylidene bromide	$C_2H_2Br_2$	ED	40
			1.86	Vinyl bromide	C_2H_3Br	ED	38, 39, 40
≡C–Br	1.829	1.805	1.789	Bromocyanide	BrCN	MS	41, 42
			1.793	Methylbromoacetylene	CH_3CCBr	MS	43, 44
⩾C–I	2.097	2.097	2.14	Butyl iodide	$(CH_3)_3Cl$	MS	22
			2.139	Methyl iodide	CH_3I	MS	35, 45
			2.139	Ethyl iodide	C_2H_5I	MS	46
>C–I	2.066	2.066	2.03	Vinyl iodide	C_2H_3I	ED	40
			2.03	Vinylidene iodide	$C_2H_2I_2$	ED	40
≡C–I	2.019	2.019	1.995	Iodocyanide	ICN	MS	41
			2.00	Iodocyanide		MS	47
			1.99	Methyliodoacetylene	CH_3CCl	MS	43

MS: Microwave spectroscopy ED: Electron Diffraction

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Discussion

It may be seen from the table that the bond lengths for a given bond environment in different molecules vary slightly. This slight variation in the carbon-chlorine and carbon-bromine bond lengths for a given bond environment in different molecules may be explained on the basis of the effect of an electronegative atom attached to the carbon atom which induces partial double-dond characters in other bonds formed by the carbon atom. It has been observed that the carbon-chlorine bond distance in $C_2H_2Cl_2$ is less than that in CH_3Cl, and that this bond distance in $CHCl_3$ is less than that in $C_2H_2Cl_2$. Brockway(19) has attributed this difference to the effect of the double-bond character of one carbon-chlorine bond induced by the partial ionic character of another carbon-chlorine bond formed by the same carbon atom. This effect of the induction of a double-bond character by the partial ionic character of another bond is much more important for fluorine-substituted molecules than for molecules containing chlorine, bromine or iodine. This is partially due to the well-known fact that the C–F bond has a larger ionic character than the other carbon-halogen bonds. This well-known shortening of carbon-fluorine bond lengths upon the addition of F-atoms is a different phenomenon and is often larger than the shortening of carbon-fluorine bond lengths with the number of adjacent atoms or bonds. Therefore, we have not included the carbon-fluorine bonds in this study.

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