A Study of Carbon-Fluorine Bond

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The interatomic distances show a linear dependence on the number of adjacent atoms or bonds. The variation in carbon-chlorine, carbon-bromine and carbon-iodine bond lengths with the environment has been explained on the basis of the hybridization effect.[1] It will be shown in this paper that the variation of carbon-fluorine bond length with the number of adjacent bonds or atoms can be adequately explained on the basis of extreme type of hybridization of carbon orbitals and this variation is approximately linearly dependent on the number of adjacent atoms or bonds. In the carbon-fluorine bond the operational changes due to introduction of fluorine atoms in the molecule are also noticeable and these changes can be adequately explained by taking into account the second order or intermediate degree of hybridization of the carbon atom. The observed bond lengths may be fairly reproduced by assigning

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[1] A. S. Rajput and S. Chandra, This Bulletin, **39**, 1854 (1966).

TABLE 1. CARBON-FLUORINE BOND LENGTHS

Bond type	Observed length in Å	Name of the substance	Formula	Ref.
→C-F	1.385	Methyl fluoride	CH_3F	(a), (b)
	1.358	Methylene fluoride	CH_2F_2	(c)
	1.335	Trifluoromethyl isocyanide	OF_3CN	(d)
	1.332	Fluoroform	CF_3H	(a), (e)
	1.317	Carbon tetrafluoride	CF_4	(f)
>C-F	1.348	Acetyl fluoride	CH_3COF	(g)
	1.347	Vinyl fluoride	$CH_2 : CHF$	(h)
	1.341	Formyl fluoride	HCOF	(i)
	1.32	1, 1-difluoroethylene	$C_2H_2F_2$	(j)
≡C-F	1.284	Fluoroacetylene	FC ⋮ CH	(k)

(a) O. R. Gilliams, H. D. Edwards and W. Gordy, *Phys. Rev.*, **75**, 1014 (1949); **76**, 195 (1949).
(b) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).
(c) D. R. Lide, Jr., *Phys. Rev.*, **87**, 227 (1952).
(d) J. Sheridan and W. Gordy, *J. Chem. Phys.*, **20**, 591 (1952).
(e) S. N. Ghosh, R. Trambarulo and W. Gordy, *ibid.*, **20**, 605 (1952).
(f) Tables of Interatomic Distances," ed. by L. E. Sutton, Special Publication No. 11, Chem. Soc., London (1958).
(g) L. Pierce and L. C. Krisher, *J. Chem. Phys.*, **31**, 875 (1959).
(h) H. W. Morgan and J. H. Goldstein, *ibid.*, **30**, 1025 (1959).
(i) P. Favero, A. M. Mirri and J. G. Baker, *Il Nuovo Cimento*, **17**, 740 (1960); O. H. LeBlanc, Jr., V. W. Laurie and W. D. Gwinn, *J. Chem. Phys.*, **33**, 598 (1960).
(j) A. Roberts and W. F. Edgell, *ibid.*, **17**, 742 (1949); *Phys. Rev.*, **76**, 178 (1949); V. W. Laurie, *J. Chem. Phys.*, **34**, 291 (1961).
(k) J. K. Tyler and J. Sheridan, *Proc. Chem. Soc.*, 119 (March 1960).

a new covalent radius of fluorine atom which is obtained by taking into account the lone pair repulsion forces and rehybridization of the fluorine atom. The values of the carbon-fluorine bond lengths and the molecules from which they have been obtained are quoted in Table 1. The quoted bond lengths are considered to be the best values available at the present time. It is seen from the Table 1 that the data confirm the earlier conclusion,[1] that the bond lengths increase linearly with the increase in the number of adjacent bonds or atoms.

Values for the radii of the hybrid orbitals of carbon have been assigned and are 0.767 Å, 0.736 Å and 0.689 Å for tetrahedral (te or sp^3), trigonal (tr or sp^2) and diagonal (di or sp) carbon atoms respectively.[1] Schomaker and Stevensen[2,3] have proposed for the single bond covalent radius of fluorine a value of 0.72 Å which is one half the interatomic distance in F_2. But the two atoms forming the bond F-F under consideration have lone pairs of electrons and these lone pairs will repel one another with the consequence that the bond between the pair of fluorine atoms is lengthened.[4] Also, the fluorine atom in passing from F_2 to any fluoro-derivative compound rehybridizes in such a way as to shorten its effective convalent radius.[5] In F_2, the fluorine atom is joined to an atom that is highly electronegative. Consequently, most of the *s*-character of the fluorine atom in F_2 is captured by the unshared electrons. In fluoro-derivatives such as CH_3F or CHF_3, however, the bonding orbitals tilt down steeply toward fluorine. This increases the demand made by the bonding electrons for *s*-character from the fluorine atom, and as the fluorine atom rehybridizes to meet this demand, the bond to carbon becomes richer in *s*-character from the fluorine side and shorter. Thus the effective covalent radius of fluorine is shortened. The average observed distance in CH_3F (Table 1) may be taken to be the normal carbon-fluorine single bond distance in which there are no lone pair repulsion effects and the fluorine atom has been rehybridized in order to meet the demand of the *s*-character by the bonding electrons. The suggested new value of the covalent radius of fluorine 0.62 Å has been obtained by subtracting the value of effective covalent radius of carbon (0.767 Å) from this carbon-fluorine bond distance. The length of a single bond between two atoms A and B can be calculated from the Schomaker and Stevenson rule.[2,3] Schomaker-Stevenson rule gives good agreement with the experiment in some instances, but in other

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2) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).
3) L. Pauling, "The Nature of the Chemical Bond," 3rd Edition, Cornell University Press, Ithaca, New York (1960).
4) J. K. Wilmshurst, *J. Chem. Phys.*, **33**, 813 (1960).
5) H. A. Bent, *ibid.*, **33**, 304 (1960).

cases the additivity rule without the correction gives better agreement.1) If the Schomaker-Stevenson rule is to be applied to carbon-fluorine bond, the long covalent radius (0.72 Å) derived from F_2 must be used. However, this long radius for fluorine includes the extension due to lone pair repulsions and other effects discussed earlier. Hence, Schomaker-Stevenson expression actually corrects for lone pair repulsion effects which exist in F_2 rather than correcting for ionicity. It has been found that with our new value of covalent radius of fluorine the Schomaker-Stevenson correction is not at all needed for C-F bonds also. The value for the te C-F bond length calculated by the addition of the radii of hybrid orbitals of carbon (0.767 Å) and the covalent radius of fluorine (0.62 Å) is 1.387 Å which agrees well with the experimental value of C-F bond length in methyl fluoride (1.385 Å). The calculated value for the trC-F bond length is 1.356 Å in agreement with the observed values in acetyl fluoride (1.348 Å) vinyl fluoride (1.347 Å) and formyl fluoride (1.341 Å). Also, the value calculated for the di C-F bond length 1.309 Å agrees fairly with the observed value in fluoroacetylene (1.284 Å). Here, we have considered only molecules with a single fluorine atom because of the tendency toward shorter bonds when several fluorine or halogen atoms are attached to the same carbon-atom.

It is also seen from the Table 1 that the bond lengths vary for the same bond environment in different molecules. This variation is about −0.025 Å for each added F atom. The average observed distance 1.385 Å in CH_3F is taken to be the normal carbon-fluorine single bond distance. A decrease of about 0.027 Å is observed for molecules with two fluorine atoms attached to the same carbon atom (1.358 Å in CH_2F_2), about 0.053 Å for molecules with three fluorine atoms (1.332 Å in CF_3H) and 0.068 Å for molecules with four fluorine atoms attached to the same carbon atom (1.317 Å in CF_4). This shortening of carbon-fluorine bond length, which occurs when fluorine atoms are introduced into the molecules, is also noticeable in the single bonds having two bonds adjacent to it ($\rangle$C-F) as is obvious from Table 1. This variation in the carbon-fluorine bond length for a given bond environment in different molecules was explained by Brockway6) on the basis of the effect of the double bond character of one carbon-fluorine bond induced by the partial ionic character of another carbon-fluorine bond formed by the same carbon atom. However, these explanations on double bonded structures have been criticized by Skinner, Sutton and Wells.7-9)

In the derivation of covalent radii of carbon atom only the extreme hybridization types sp, sp^2 and sp^3 were considered, although intermediate degrees of hybridization are also possible. We have examined the possibility to explain, qualitatively, these variations in bond lengths on the basis of intermediate or second order hybridization10) of the carbon atom. Walsh11) has suggested that " If a group X attached to carbon is replaced by a more electronegative group Y, then the carbon valency toward Y has more 2p character than it had towards X." In other words, the replacement in the structure B-C-X of X by an atom Y, more electronegative than X, causes atom C to divert *s*-character from the bond to Y to the orbital toward B thus causing the adjacent B-C bond to become shorter. A direct and strong evidence of this is achieved from the spin-spin coupling constants between protons and ^{13}C nuclei. Muller and Pritchard12) have pointed out that the coupling constants $J(^{13}C\text{–}H)$ for hydrocarbons depend mainly on the extent of sp hybridization of the carbon atomic orbitals used in the bonds and have established the following linear relationship between the values of $J(^{13}C\text{–}H)$ and the corresponding fractional *s*-character, α^2_H, of the *c*-orbital bonding to H:

$$J(^{13}C\text{–}H)=500\ \alpha^2_H$$

Accordingly, from the $J(^{13}C\text{–}H)$ coupling constants for the series CH_3F, CH_2F_2 and CHF_3 of 149.1, 184.5 and 239.1 sec^{-1} respectively13) it is evident that there is more carbon *s*-character in the orbital toward hydrogen in CHF_3 than in CH_2F_2 and more in the latter than in CH_3F. Carbon uses four very nearly of sp^3 type orbitals in CF_4 while in CHF_3 the large difference in the electronegativity between hydrogen and fluorine causes the carbon atom to concentrate its *s*-character preferentially in the C–H bond at the expense of C–F bond which therefore becomes richer in the *p*-character from the carbon side and hence longer than that in CF_4. From the $J(^{13}C\text{–}H)$ coupling constants of fluoromethanes carbon *s*-character in the orbital toward fluorine atom can readily be computed if carbon *s*-character in the orbital toward hydrogen is known and the carbon atomic orbitals (AO's) are required to be orthogonal. This carbon *s*-character in the orbital toward fluorine calculated from coupling constants is 10, 13 and 17 per cent for CH_3F, CH_2F_2 and CHF_3 molecules respectively. Thus, the C–F bond becomes richer in *s*-character from carbon to fluorine side and hence shorter as the more fluorine atoms are attached to the same carbon atom. It

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6) L. O. Brockway, *J. Phys. Chem.*, **41**, 185 (1937).
7) H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944).
8) T. L. Cottrell and L. E. Sutton, *Quart. Revs., London*, **2**, 260 (1948).
9) A. F. Wells, *J. Chem. Soc.*, **1959**, 55.
10) W. Moffitt, *Proc. Roy. Soc. (London)*, **A202**, 534, 548 (1950).
11) A. D. Walsh, *Dissussions Faraday Soc.*, **2**, 18 (1947).
12) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).
13) S. G. Frankiss, *J. Phys. Chem.*, **67**, 752 (1963).

may also be mentioned here that from the fluorine side, the F_3C–F bond is richer in *s*-character than the H_3C–F bond because the electronegativity of the group CF_3(2.32) is smaller than that of group CH_3-(2.42)[14] according to the rule that an atom tends to concentrate its *s*-character in orbitals towards electropositive group. However, this will not be of much importance as far as the C–F bond is concerned because the effective covalent radius of fluorine is not so strongly dependent on hybridization as that of carbon atom.

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14) S. Chandra and S. Chandra, *Tetrahedron,* **22,** 3403 (1966).