the fruit in the previous study. With the samples collected at 14 and 21 days after treatment it had been found that 1 μg IA/ml homogenate gave approximately the same dehydrogenase activity as that from fruits treated with 200 ppm ClPA. The results of this study are presented in Table 2. The control homogenates in this case were the same as those for the ClPA-treated fruits, with aliquots from each replication removed for treatment *in vitro* with IA. The reduction of TTC by the various dehydrogenase systems in the presence of malate, fumarate, succinate, and glutamate when treated with varying amounts of IA *in vitro* corresponds closely to that found when fruits are treated on the plant with proportional amounts of ClPA (Figs. 1 and 2).

The evidence seems to support the hypothesis put forth by Thimann and others (*2–6*) that the effect of growth regulators of the auxin type is exerted through dehydrogenase enzyme systems. It has recently been pointed out by Brodie and Gots (*11*) that the actual donor of hydrogen in the reduction of TTC appears to be a flavin enzyme through a dehydrogenase-DPN-flavoprotein system. Since it may be assumed that an enzyme of the flavin type is present in the tomato homogenates, any increase in dehydrogenase activity should be manifested by an increased rate of reduction of TTC, unless, of course, the rate of oxidation of DPN by the flavin enzyme is limiting. At present this does not seem to be the case; however, a further investigation of this aspect is being conducted.

References

1. Hsiang, T. T. *Plant Physiol.*, **26**, 708 (1951).
2. Thimann, K. V. In F. Skoog (Ed.), *Plant Growth Substances.* Madison: Univ. Wisconsin Press (1951).
3. Commoner, B., and Thimann, K. V. *J. Gen. Physiol.*, **24**, 279 (1941).
4. Berger, J., and Avery, G. S. *Am. J. Botany*, **33**, 290 (1943).
5. ———. *Science*, **98**, 454 (1943).
6. ———. *Am. J. Botany*, **31**, 11 (1944).
7. Murneek, A. E., Wittwer, S. H., and Hemphill, D. D. *Proc. Am. Soc. Hort. Sci.*, **45**, 371 (1944).
8. Murneek, A. E. *Ibid.*, **50**, 254 (1947).
9. Kun, E., and Abood, L. G. *Science*, **109**, 144 (1949).
10. Isenberg, F. M. R., *et al. Ibid.*, **113**, 58 (1951).
11. Brodie, A. F., and Gots, J. S. *Ibid.*, **114**, 40 (1951).

Manuscript received February 11, 1952.

Carbon—Carbon Bond Lengths

R. T. Sanderson[1]

Department of Chemistry and Chemical Engineering, State University of Iowa, Iowa City

A method of estimating bond lengths and a system of classifying bonds according to length have recently been outlined (*1, 2*). The purpose of this paper is to discuss in more detail some specific applications to carbon—carbon bonds.

The existence of separate groups of carbon—carbon bond lengths within the broad limits of about 1.15 to 1.60 A had previously been pointed out by A. F. Johnson (*3*).

Since the earlier work (*1, 2*), it has seemed preferable to assign somewhat larger "nonpolar covalent radii" to the inert atoms (*4*). These have resulted in somewhat larger stability ratio (SR) values—e.g., 5.75 for fluorine, 3.79 for carbon, and 3.55 for hydrogen—but the revised values do not affect the bond length calculations significantly, as the interrelationships remain largely unchanged. The revised values, however, are the basis of the work reported here.

TABLE 1

Some Calculated and Observed C—C Bond Lengths in Fluorocarbons

Compound	R obs (*5*)	R calc (*1*)	R obs–R calc
C_2F_6	1.45–0.06	1.40	0.05
	1.52–1.62	1.40	0.12–0.22
C_3F_6 hexafluoropropene	1.52	1.40	0.12
C_4F_8 octafluorocyclobutane	1.60–0.04 (*6*)	1.40	0.20

Single bonds. Most carbon—carbon single bonds are in general quite similar in length and show no unusual characteristics. There are two forms of deviation from "expected" length, however. The first is in molecules wherein two singly linked carbon atoms are each joined to highly electronegative atoms, so that the adjacent carbon atoms must be of like positive charge, in accordance with the stability ratio theory (*1*), or any theory admitting bond polarity. In such molecules the carbon—carbon bonds are longer than otherwise expected. The second form of deviation is a bond "shortening" when the carbon atoms joined in the single bond are linked to other atoms by multiple bonds.

The first type is illustrated by the fluorocarbons. As shown in Table 1, the reported C—C distances are the same as, or slightly greater than, in paraffin hydrocarbons, whereas according to the stability ratio theory, they should be about 0.14 A shorter. It is suggested that if the theory is correct in this application, the observed absence of shortening may be chiefly the result of repulsion between the like charged carbon atoms. This should result in weakening of the bond. However, the fluorocarbons are noted for their thermal stability (*7*). It is suggested that the polarity of the C—F bonds is sufficiently great, and the fluorine atoms are sufficiently close to the carbon atoms next to the carbon atom to which they are attached, that an appreciable electrostatic attractive force is exerted between each positive carbon atom and the negative fluorine atoms that are attached to the next carbon atom. This force would add to the stability of the fluorocarbon molecule, compensating for the loss in stability resulting from carbon—carbon repulsion. One would expect the potential hindrance to free rotation about the C—C bonds in such molecules to be unaffected by this attractive force but increased by repulsion among the negative fluorine atoms attached to adjacent carbon atoms. This hindrance has been

---

[1] Thanks are due to Jack F. Mills and Wesley W. Wendlandt for assistance in some of the calculations necessary for this work.

determined as 4350 cal/mole for hexafluoroethane, C_2F_6 (*8*), compared to 3000 cal/mole for ethane (*9*).

Illustrating the shorter-than-expected bonds are single bonds between two double-bonded carbon atoms, which are classified as type IIa (*1*), being 0.923 times the normal single bond in length. The only examples reported are 1,3-butadiene and cyclopentadiene. An equivalent single bond should be that between an olefinic carbon and a ring carbon in stilbene (1,2-diphenylethylene); this bond is in the same class. The calculated–reported bond lengths in these molecules are 1.44–1.47 (*5*), 1.44–1.46 (*5*), and 1.44–1.44 A (*10*).

Single bonds to triple-bonded carbon are of the same type, as evidenced by 14 different reported examples (*1*). Single bonds between two triple-bonded carbons, however, are still shorter, being classified as IIb (*1*), using the factor 0.885 times the normal single bond length. The only three examples cited in the literature appear to be in hydrocarbons with the structural skeletons $\mathrm{C{-}C{\equiv}C{-}C{\equiv}C{-}C}$ and $\mathrm{C{\equiv}C{-}C{\equiv}C}$, and in cyanogen, $\mathrm{N{\equiv}C{-}C{\equiv}N}$. The calculated–reported (*11*) bond lengths are 1.38–1.38, 1.38–1.36, and 1.33–1.37 A.

These types are illustrated by the interesting example of pirylene, a hydrocarbon having the skeleton $\mathrm{C{-}C{\equiv}C{-}C{=}C}$. The first bond is a single bond to a triple-bonded carbon, and the second is a triple bond, type IVa, for which the factor 0.770 is used. The third, between a double and a triple bond, may be regarded as an average of IIa and IIb. (Similar bonds occur in "tolane," diphenyl acetylene, with lengths calculated on this basis as 1.41, comparable to 1.40 A reported [*10*].) The fourth bond of pirylene is an ordinary olefinic double bond. The calculated–reported (*12*) bond lengths are 1.44–1.47, 1.20–1.20, 1.41–1.42, and 1.32–1.35 A.

A single bond between two double bonds is, then, an average in length of an ordinary single bond and a double bond. Similarly, a single bond between two triple bonds is an average of an ordinary single bond and a triple bond.

Multiple bonds. Carbon—carbon double bonds and carbon—carbon triple bonds are evidently nearly all of the same types, being equal to the single bond length times the factors 0.845 and 0.770. The only reported exceptions are the halogen-substituted derivatives, in which the C—C bond lengths are greater than expected after correction for electronegativity adjustment (*1*). It is of interest that these molecules are like the fluorocarbons in having adjacent carbon atoms of like charge. The observed bond "lengthening" may possibly be explained similarly as resulting from repulsion between the like charged carbon atoms.

The bonds in aromatic rings are especially interesting. The ideas described earlier (*1*) are very useful in providing a simple explanation of the fact that the carbon—carbon distance in benzene is shorter than an average of an ordinary single bond and a double bond. As discussed above, a single bond between two double-bonded carbon atoms is shorter than an ordinary single bond, being of type IIa instead of Ia, and hence only 0.923 as long. Since the bonds in a benzene ring are all alike, their length should be the average of IIa and IIIa, not Ia and IIIa. The factor is then 0.885 (which, incidentally, also represents the average of a triple bond and an ordinary single bond). The Ia bond length in benzene is 1.58 A, and 1.58 × 0.885 is 1.40, comparable to the reported (*13*) bond length of 1.39 A. The higher-than-expected bond energy is of course consistent with the shorter length. The C—C distances in pyridine and pyrazine, as well as for phenyl compounds, in all 15 examples reported in the literature (*5*), are in the same length class as those of benzene.

With the exception of bonds between atoms of considerable like charge, which are expected to be longer, one may then estimate the carbon—carbon distance in any organic molecule, preferably in the vapor phase, as the product of the calculated single bond length (*1*) and a factor, as summarized in Table 2. The more important significance of this work seems to arise not from the method of deriving the factors (*1*), which was of necessity oversimplified, but from the very existence of such factors, by which the several bond lengths, within the limits of experimental error, appear to indicate definite bond types, which are related simply and definitely.

TABLE 2

Carbon—Carbon Bonds, Factors, and Lengths

Bond type	Factor (1–0.0385n)	*n*	Length, if calc single bond is 1.52–1.58 A
Ia Ordinary single	1.000	0	1.52–1.58
IIa Single between two doubles Single to triple (Graphite)	0.923	2	1.40–1.46
IIb Single between two triples Aromatic ring	0.885	3	1.35–1.40
IIIa Double	0.845	4	1.29–1.34
IVa Triple	0.770	6	1.17–1.22

References

1. Sanderson, R. T. *Science,* **114**, 670 (1951).
2. ———. *J. Am. Chem. Soc.,* **74**, 272 (1952).
3. Johnson, A. F. *Science,* **112**, 503 (1950).
4. Sanderson, R. T. *J. Chem. Phys.,* **20**, 535 (1952).
5. Allen, P. W., and Sutton, L. E. *Acta Crystallog.,* **3**, 46 (1950). (See for original references.)
6. LeMaire, H. P., and Livingston, R. L. ACS 117th Mtg., Detroit (Apr. 1950).
7. Grosse, A. V., and Cady, G. H. *Ind. Eng. Chem.,* **39**, 367 (1947).
8. Pace, E. L., and Aston, J. G. *J. Am. Chem. Soc.,* **70**, 566 (1948).
9. Kemp, J. D., and Pitzer, K. S. *Ibid.,* **59**, 276 (1937).
10. Wells, A. F. *Structural Inorganic Chemistry,* 2nd ed. New York: Oxford Univ. Press, 53 (1950).
11. Pauling, L., Springall, H. D., and Palmer, K. J. *J. Am. Chem. Soc.,* **61**, 927 (1939).
12. Spurr, R. A., and Schomaker, V. *Ibid.,* **64**, 2693 (1942).
13. Schomaker, V., and Pauling, L. *Ibid.,* **61**, 1769 (1939).

Manuscript received January 28, 1952.