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A SURVEY OF CARBON–CARBON BOND LENGTHS

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Abstract—The operational definitions of bond length are discussed. The importance of using bond lengths determined by the same experimental method when looking for small variations is emphasized. A survey is given of recent measurements of C—C and C=C bonds and of the various types of CC single bonds. The single bond lengths may be fitted by a set of orbital radii which depend on the hybridization state of the carbon atom. Bonds between carbon and nitrogen, oxygen, fluorine, chlorine, and silicon are also discussed. While variations in CC bond lengths can be satisfactorily explained on the basis of hybridization being the major factor, it appears necessary to introduce electron delocalization effects when atoms with lone pairs are involved. It is shown that bond angles do not provide a reliable measure of the carbon hybridization.

INTRODUCTION

It is probably fair to say that bond lengths have been more widely used than any other molecular property for providing an insight into the nature of the chemical bond. Even with very crude measurements of bond length, it has been possible to detect some of the gross effects of molecular environment upon the bond between two given atoms. As theories of molecular structure have been refined, there has been a tendency to attach significance to smaller and smaller variations in measured bond lengths. While experimental techniques have improved concurrently, the correspondence has not always been one-to-one. In the case of carbon–carbon bond lengths in particular it appears that the experimental uncertainties have not always been fully appreciated. As an example it is only necessary to cite ethane, where an observed CC distance of 1·543 Å has long held the status of an absolute standard for the paraffinic CC bond. While many authors have taken this value to be accurate to 0·001 Å, improved measurements during the last three years have shown the correct distance to be 0·010–0·020 Å shorter. Furthermore, the precision of measurement of this and many other bond distances is now sufficiently high that it is necessary to consider the operational definition of the distance obtained by each experimental technique.

While ambiguities of 0·01–0·02 Å are small in an absolute sense, they are not much smaller than some of the bond-length variations which are regarded as theoretically significant. In this paper we shall discuss some of the difficulties in comparing carbon–carbon distances and afterwards review the status of measurements on different types of CC bonds. Some implications of the present measurements will also be pointed out.

THE MEANING OF MEASURED BOND LENGTHS

An ideal measurement of a bond length would provide a value for r_e, the distance between the two nuclei in the hypothetical vibrationless state of the free molecule. Any practical measurement, of course, will yield a distance which is averaged over the vibrational motion of the nuclei. It is clear that the nature of this averaging is not identical for the two principal methods of measurement, spectroscopy and electron diffraction. With sufficient knowledge of the vibrational motion we might hope ultimately to be able to correct the average distances determined by each method to equilibrium values. While some progress is being made in this direction, we are at present unable to make this correction with confidence for any but the very simplest molecules. It is therefore important to examine the validity of comparing experimental bond lengths determined in different ways.

An analysis of the rotational spectrum of a molecule yields the three rotational constants a_0, b_0, c_0 for the ground vibrational and electronic state. It is customary to define ground-state moments of inertia as the reciprocals of these constants, viz., $I_a^0 = \hbar^2/2a_0$, etc. It is well known that I_a^0 differs in a very complicated way from I_a^e, the moment calculated from the equilibrium co-ordinates r_e; since the rotational constants include a contribution from Coriolis interactions with excited states, it is not in general possible to express I_a^0 as an explicit average over the vibrational co-ordinates. In only a few cases, outside of diatomic molecules, is there enough information available to obtain accurate values of the I^e's. Consequently, most structures determined by spectroscopic methods have been of the so-called r_0 type. We may define an r_0 structure as a set of geometric parameters which reproduce the observed values of I_a^0, I_b^0, I_c^0 for the molecule. Such a structure is uniquely defined for diatomic molecules and for a few special polyatomic types such as linear XY_2 and tetrahedral XY_4 molecules. However, when we advance to the slightly more complicated case of a bent XY_2 molecule, the r_0 structure is no longer unique, since one can calculate three structures from the moments of inertia which will not be identical because of the finite inertial defect. When the number of independent structural parameters exceeds three, we must use the ground-state moments of more than one isotopic species (or else assume some of the parameters) in order to obtain the r_0 structure. Since the change of mass affects the vibrational motion as well, the resulting structure will depend upon our choice of isotopic species—a choice which in practice has often been dictated by natural isotopic abundances or the ease of chemical synthesis. Numerous examples have been given of r_0 structures which vary over a range of 0·01–0·02 Å when different combinations of isotopic species are used in the calculation. To reduce this problem, many investigators have studied more isotopic species than necessary and used a least squares procedure to obtain the "best" structure. However, the result is still dependent on the choice of imput data, and it is always difficult to assess the real uncertainties in such a structure.

We must conclude, then, that the r_0 structure is a rather fuzzily defined concept. This does not imply that r_0 structures are useless; indeed, in simple molecules the distance between heavy atoms is often relatively insensitive to the choice of data for the calculation. However, the lack of an unambiguous operational definition, and the consequent difficulty in estimating the probable errors, makes r_0 structures fundamentally unsuitable for the detection of small differences in bond distances. In an effort to avoid these problems Costain[1] has proposed the use of r_s or "substitution" structures. The r_s co-ordinates of a given atom in a molecule are determined by the isotope *shifts* in the moments of inertia when that atom (and no others) is substituted. A complete r_s structure thus requires single isotopic substitutions on every atom. The r_s parameters will not reproduce the ground-state moments I_a^0, I_b^0, I_c^0, but generally give calculated moments which are smaller. From this and other arguments Costain[1] has shown that the r_s parameters usually provide a closer approximation to the r_e's

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[1] C. C. Costain, *J. Chem. Phys.* 29, 864 (1958).

than do the r_0's. The exact relation between r_s and r_e is not yet understood for polyatomic molecules. However, the important advantage of the r_s structure lies in its unambiguous operational definition, which can be demonstrated by two tests: (1) in overdetermined systems different species may be used as the starting point for the isotopic substitutions, and the resulting r_s co-ordinates generally agree to 0·001 Å or better; (2) in molecules which have an axis or plane of symmetry one obtains essentially the same r_s parameters (at least for heavy atoms)[2] regardless of what combination of moments is used.[3] The most serious difficulty occurs when an atom is close to a principal inertial axis; in such a case the r_s co-ordinate is unreliable because of vibrational effects, and some other technique must be used. However, if we exclude these unfavorable examples (which are easily recognized), the self-consistency of r_s bond lengths to a precision of 0·001–0·002 Å or better has been demonstrated in a variety of molecules. We can therefore have considerably more confidence in comparing bond lengths in a series of molecules when they are all determined by the substitution method.

Interatomic distances measured by electron diffraction are generally reported either as r_m values, obtained from the maxima in the radial distribution curve, or r_g values, which are based on the centers of gravity of the peaks in the curve. The importance of specifying the type of distance which is reported has been emphasized by Bartell[4]. There is some evidence to indicate that r_g distances, at least when measured in the same laboratory, are suitable for precise comparison of bond lengths. For example, the CC distances in the normal hydrocarbons from butane through heptane,[5] where there is no reason to expect any significant difference in r_g values, fall in the range 1·531–1·534 Å (with a stated experimental uncertainty of 0·002 Å). However, an independent value of 1·539 ± 0·002 Å has also been reported for n-butane.[6]

If we tentatively accept that the electron-diffraction r_g distances provide a self-consistent set of bond lengths which may be compared among themselves, there remains the problem of their relation to the spectroscopic r_s distances. Unfortunately, there are not many examples where an accurate comparison can be made. In the case of saturated hydrocarbons, the r_s carbon-carbon distances in propane[7] and isobutane[8] are 1·526 ± 0·002 Å. Only an r_0 distance is available for ethane, but a rough correction[8] suggests that the r_s distance is in the range 1·525–1·530 Å. The r_g distance in the higher paraffins[5] is 1·533 ± 0·002 Å (with an alternative value of 1·539 Å), and 1·538 Å has been reported for ethane.[9] Therefore, it appears that r_g values for the CC distance are larger than the r_s values by something like 0·005–0·010 Å. Similarly, the r_g CH distances in the higher paraffins (an average of methyl and methylene groups) range from 1·108 to 1·121 Å, while in propane the methylene CH bond has an r_s length of 1·096 ± 0·002 Å, and the methyl CH bond is even shorter. There seems little doubt that these differences are outside the experimental precision of the respective methods.

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[2] This is not always true for hydrogen atoms. There is particular difficulty when an atom is involved in a large-amplitude vibration, e.g. the torsional motion of a methyl group (see ref. 7).

[3] This means, for example, that the relation $\Delta I_a^\circ + \Delta I_b^\circ - \Delta I_c^\circ = 0$ is usually satisfied to a good approximation when an isotopic substitution is made in a planar molecule, while $I_a^\circ + I_b^\circ - I_c^\circ \neq 0$ because of zero-point vibrational effects.

[4] L. S. Bartell, *J. Chem. Phys.* 23, 1219 (1955).

[5] R. A. Bonham, L. S. Bartell and D. A. Kohl, *J. Amer. Chem. Soc.* 81, 4765 (1959).

[6] K. Kuchitsu, *Bull. Chem. Soc. Japan* 32, 748 (1959).

[7] D. R. Lide *J. Chem. Phys.* 33, 1514 (1960).

[8] D. R. Lide, *J. Chem. Phys.* 33, 1519 (1960)

[9] A. Almenningen and O. Bastiansen, *Acta Chem. Scand.* 9, 815 (1955); corrected to an r_g value in ref. 5

At the present time, then, several distinct types of bond distances are being reported, and these may differ from each other by considerably more than the strictly experimental uncertainties. Until it is possible to reduce these distances to some common denominator (preferably r_e) without too great a loss of accuracy, it is desirable to restrict oneself to a single type when comparing bond distances in different molecules. Even here, of course, one is tacitly assuming that r_s (or r_0, as the case may be) bears some constant relation to r_e; i.e. that the vibrational pattern does not differ markedly from one molecule to another. This is probably not too bad an assumption in the case of hydrocarbons, although its effect on methyl-group structures might be important.

With these problems in mind, we shall attempt a critical survey of the experimental results on the lengths of CC bonds of various types. Aromatic compounds will not be discussed because of the limited amount of data. Most of the comparisons will be made among r_s values, but r_e distances will be quoted when available.

C=C AND C≡C BONDS

There is now complete agreement that the C=C distance in ethylene, regardless of the method of measurement, is about 0·02 Å shorter than the 1·353 Å value which has been accepted for many years. Spectroscopic r_0 values of 1·337 ± 0·003 Å (infrared)[10] and 1·339 ± 0·003 Å (rotational Raman)[11] have been recently reported. We can estimate that the r_s distance is probably 1·330–1·335 Å; it is very unlikely to be less than 1·330 Å. Some reported r_s values in ethylene derivatives are 1·336 ± 0·004 Å in propylene,[12] 1·332 ± 0·002 Å in vinyl chloride,[13] 1·329 ± 0·006 Å in vinyl fluoride,[14] 1·325 ± 0·002 Å in 1,2-difluoroethylene,[15] 1·339 Å in vinyl cyanide[16] and 1·347 ± 0·003 Å in vinyl silane.[17] There appears to be a tendency for halogen substitution to decrease the C=C distance slightly,[16] and the vinyl silane distance is higher than the other examples; otherwise, the variations among these compounds are probably not significant. We can adopt 1·335 ± 0·010 Å as the characteristic r_s value for the C=C distance.

The constancy of the C=C distance is also supported by electron diffraction results. Some reported values are 1·333 ± 0·002 Å in ethylene,[18] 1·331 ± 0·003 Å in isobutylene[19] and 1·337 ± 0·005 Å in 1,3-butadiene.[20]

The r_s length of the C≡C triple bond has been accurately determined in methyl acetylene[1] (1·206 Å) and cyanoacetylene[1] (1·205 Å). The precision of these values should be about 0·001 Å. A somewhat less accurate value of 1·209 Å has been reported for propynal,[21] HC≡CCHO. In acetylene[22] itself r_0 = 1·207 Å and r_e = 1·205 Å. The constancy of the C≡C bond length at about 1·206 Å is therefore well-established.

[10] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.* 80, 2673 (1958).

[11] J. M. Dowling and B. P. Stoicheff, *Canad. J. Phys.* 37, 703 (1959).

[12] D. R. Lide and D. Christensen, *J. Chem. Phys.* to be published.

[13] D. Kivelson, E. B. Wilson and D. R. Lide, Jr., *J. Chem. Phys.* 32, 205 (1960).

[14] Calculated from data of B. Bak, D. Christensen, L. Hansen-Nygaard and J. Rastrup-Andersen, *Spectrochim. Acta* 13, 120 (1958); H. W. Morgan and J. H. Goldstein *J. Chem. Phys.* 30, 1025 (1959).

[15] V. W. Laurie, *J. Chem. Phys.* 34, 291 (1961).

[16] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* 30, 777 (1959).

[17] J. M. O'Reilly and L. Pierce, *J. Chem. Phys.* 34, 1176 (1961).

[18] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* 31, 400 (1959).

[19] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* 32, 824 (1960).

[20] A. Almenningen, O. Bastiansen and M. Trætteberg, *Acta Chem. Scand.* 12, 1221 (1958).

[21] C. C. Costain and J. R. Morton, *J. Chem. Phys.* 31, 389 (1959).

[22] J. H. Callomon and B. P. Stoicheff, *Canad. J. Phys.* 35, 373 (1957).

The most accurate measurements available at this time indicate that any lengthening of double and triple bonds by conjugation must be extremely small—certainly less than 0·010 A and probably not over 0·005 Å. This result is consistent with most current theories. Even when conjugation is assumed to affect other molecular properties in an important way, recent calculations[23] indicate that multiple-bond lengthening should be the order of 0·005 Å or less.

C—C SINGLE BONDS

The near-constancy of the length of carbon–carbon single bonds of a given bond type has been pointed out many times.[16,24] We shall review the most recent measurements to see the extent to which this constancy is confirmed and to establish the best values for the various bond types. The symbols[23] *te*, *tr*, *di* will be used to indicate carbon atoms with hybridization sp^3, sp^2, sp, respectively. All distances are r_s values unless otherwise stated.

te–te. Two reliable r_s values are available for saturated hydrocarbons, 1·526 ± 0·002 Å in propane[7] and 1·525 ± 0·002 Å in isobutane.[8] It has already been mentioned that the estimated r_s distance in ethane is consistent with these. We shall adopt 1·526 ± 0·002 Å as the standard *te–te* distance.

te—tr. The best measurements of this bond length are 1·501 ± 0·004 Å in propylene,[12] 1·503 ± 0·003 Å in acetyl fluoride,[25] 1·490 ± 0·010 Å in acetyl cyanide,[26] and 1·500 ± 0·005 Å in acetaldehyde.[27] The acetaldehyde distance comes from an r_0 structure, but a recalculation shows that r_s probably does not differ by more than 0·005 Å. An r_0 distance of 1·507 Å has been found in isobutylene.[15] The agreement among these molecules is satisfactory, and it is reasonable to adopt a representative distance of 1·501 ± 0·004 Å.

The difference between the *te–te* and *te–tr* bond lengths is thus 0·025 Å, with an uncertainty of about 0·006 Å. The electron diffraction (r_g) result for the *te–tr* bond in isobutylene[19] is 1·505 ± 0·003 Å, which is 0·028 ± 0·005 Å shorter than r_g for the *te—te* bond.[5] This close agreement on the *difference* in bond lengths is encouraging. It has long been recognized that the *te–tr* bond is shorter, but previous estimates of the amount of this shortening were about twice as large as the present value.

te–di. Good determinations have been made[1] on methyl acetylene (1·459 Å) and methyl cyanide (1·458 Å). We may adopt a value of 1·459 ± 0·002 Å.

tr–tr. There is unfortunately no r_s value available for this bond type. A spectroscopic (r_0) structure has been reported for *s-trans* acrolein,[28] $H_2C{=}CH{-}CHO$; however, this structure is far from unique since only one isotopic species was studied. The reported C—C length of 1·45 Å is probably too low, since the C=C distance used (1·36 Å) is undoubtably too high. In 1,3-butadiene[30] the electron-diffraction value for the *tr–tr* distance is 1·483 ± 0·010 Å. One might *guess* that the r_s distance is 1·47–1·48 Å.

tr–di. Values of 1·426 Å in vinyl cyanide[16] and 1·447 Å in propynal[31] ($HC{\equiv}CCHO$) have been reported. Both distances are stated to be accurate to ± 0·001 Å. However, this appears to be somewhat optimistic, since one atom in each molecule is rather close

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[23] R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).

[24] G. Herzberg and B. P. Stoicheff, *Nature, Lond.* 175, 79 (1955).

[25] L. Pierce and L. C. Krisher, *J. Chem. Phys.* 31, 875 (1959)

[26] L. C. Krisher and E. B. Wilson, *J. Chem. Phys.* 31, 882 (1959).

[27] R. W. Kilb, C. C. Lin and E. B. Wilson, *J. Chem. Phys.* **26**, 1695 (1957).

[28] R. Wagner, J. Fine, J. W. Simmons and J. H. Goldstein, *J. Chem. Phys.* **26**, 634 (1957).

to a principal axis. An uncertainty of about 0·004 Å is perhaps a more realistic estimate. Even so, there is no doubt that the bond length differs in the two molecules, and a still larger value, 1·466 ± 0·010 Å, has been obtained for acetyl cyanide.[26] Costain and Morton[21] have suggested that the replacement of $-CH_2$ by $-O$ tends to lengthen the adjacent C–C single bond by 0·02 Å; however, no such effect is noticed when propylene is compared with the acetyl compounds (see above). We cannot select a standard value for the *tr*–*di* bond length, but must accept a range from 1·42 to 1·46 Å.

di–*di*. Only one r_s value is available, 1·378 ± 0·001 Å in cyanoacetylene.[1] The r_0 length in diacetylene,[22] 1·376 ± 0·002 Å for an assumed C≡C length of 1·205 Å, is consistent with this.

TABLE 1. C–C SINGLE BOND LENGTHS (r_s VALUES)

Type	Obs. length[a] (Å)	Calculated length	
		Set A	Set B
te–*te*	1·526 ± 0·002	1·526	(1·526)[f]
te–*tr*	1·501 ± 0·004	1·506	(1·501)[f]
te–*di*	1·459 ± 0·002	1·454	(1·459)[f]
tr–*tr*	(~1·47–1·48)[b]	1·486	1·476
tr–*di*	1·426 ± 0·004[c] 1·445 ± 0·004[d] 1·466 ± 0·010[e]	1·434	1·434
di–*di*	1·378 ± 0·001	1·382	1·392
Radii:			
ρ_{te}		0·763	0·763
ρ_{tr}		0·743	0·738
ρ_{di}		0·691	0·696

[a] See text for molecules used.
[b] No r_s value available: estimate is based on electron diffraction result for 1,3-butadiene.
[c] Vinyl cyanide.
[d] Propynal.
[e] Acetyl cyanide.
[f] Used to calculate radii.

COVALENT RADII FOR CARBON

Several efforts have been made[29-31] to explain the characteristic lengths of the various C–C bond types in terms of a set of covalent radii which depend on the state of hybridization of the carbon atom. It is of interest to review this procedure in the light of the more accurate data now available. We wish to find three radii—ρ_{te}, ρ_{tr}, and ρ_{di}—which reproduce the characteristic lengths discussed in the last section (these are collected in Table 1 under "Obs. length"). The best overall fit is obtained with the radii listed under "Set A" in Table 1. With the exception of acetyl cyanide, which will be anomalous in any calculation, the mean deviation for this fit is 0·005 Å.

An alternative procedure is to assume that the bonds which involve a *te* carbon

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[29] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* 5, 166 (1959).
[30] G. R. Somayajulu, *J. Chem. Phys.* 31, 919 (1959).
[31] H. J. Bernstein, *J. Phys. Chem.* 63, 565 (1959).

atom can be characterized by a set of well-defined covalent radii—i.e. that hyperconjugation has a negligible effect on bond length. We can use the observed lengths of the *te—te*, *te—tr*, and *te—di* bonds to calculate these radii ("Set B" of Table 2) and then predict the remaining bond lengths. The *di—di* bond is seen to be 0·014 Å shorter than predicted, while for *tr—di* bonds, the distance in vinyl cyanide is 0·008 Å less, and that in propynal 0·011 Å greater (each ± 0·004 Å) than the predicted value. If we accept the electron-diffraction result on butadiene,[20] it is unlikely that the *tr—tr* bond, where we have no r_s value at present, differs very much from the predicted length of 1·476 Å. If we now wish to ascribe the differences between predicted and observed lengths to conjugation, its contribution need not be very large—roughly 10 per cent of the total shortening relative to the paraffinic bond is sufficient. Thus there is no contradiction with our premise that hyperconjugation is negligible. Furthermore, some other effect, perhaps electronegativity differences, of comparable importance to conjugation must be brought in to explain the observed variations in *tr—di* lengths.

The most accurate measurements available at this time confirm that the six C—C bond types can be "explained" with almost complete satisfaction by a set of three empirical radii. The interpretation of these radii is another matter. If we follow the ideas of Dewar and Schmeising[29], they may be regarded as characteristic covalent radii for carbon orbitals in different states of hybridization. The ratio of the differences $(\rho_{te} - \rho_{tr}):(\rho_{tr} - \rho_{di})$ is 0·025:0·042 with set B and 0·020:0·052 with set A. This agrees satisfactorily with the 1:2 ratio to be expected if one assumes that ρ is a linear function of the percentage of s character in the orbital.[29] A slightly more sophisticated calculation using expressions given by Coulson[32] predicts a ratio of 1:1·87. If one wishes to incorporate conjugation and polarity effects into this scheme in order to explain the slight deviations in Table 1, it is only *necessary* to treat them as minor factors whose contributions are of the order of 0·01 Å. Of course, it is possible that a larger contribution from electron-delocalization effects has been absorbed into the empirical radii. However, it seems less likely that a good fit in terms of empirical radii could be obtained if these resonance effects were the dominant factor, since they should be fairly sensitive to the molecular structure.

These conclusions are based upon the structures of a limited number of molecules, and they may have to be modified as more information becomes available. There is still a need for accurate measurements of CC bond lengths in a wide variety of compounds.

APPLICATION TO OTHER BONDS

It is natural to enquire whether the empirical radii derived in the last section permit any correlations of bond lengths involving carbon and another atom. Unfortunately, the reliable experimental data are somewhat limited, and it is necessary to mix bond lengths determined by different methods in order to make useful comparisons. Therefore, we cannot attach much significance to variations of less than 0·02 Å. We shall first survey the experimental results. Only bonds which are considered "single" in the zeroth approximation will be discussed.

Carbon-nitrogen bonds. Spectroscopic (r_0) values for *te* carbon are 1·474 Å in methylamine[33] and 1·472 ± 0·008 Å in trimethylamine.[34] The best example for *tr*

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[32] C. A. Coulson, *Valence* p. 206. Oxford University Press, London (1953).
[33] D. R. Lide, *J. Chem. Phys.* 27, 343 (1957).
[34] D. R. Lide and D. L. Mann, *J. Chem. Phys.* **28**, 572 (1958).

carbon is formamide, where two r_0 values, 1·343 Å[35] and 1·376 Å[36] have been reported. Further work will be necessary to establish a satisfactory structure for formamide, but we are probably safe in taking the C—N distance as 1·36 ± 0·02 Å. In cyanamide the N ··· N distance of 2·507 Å is well determined[37]; since C≡N distances are always close to 1·16 Å, we can adopt a value of 1·35 ± 0·02 Å for the *di* C—N distance.

Carbon-oxygen bonds. Some reported values for the *te* C—O bond are 1·427 ± 0·007 Å (r_0) in methyl alcohol,[38] 1·417 Å (r_0) in dimethyl ether,[39] and 1·437 ± 0·010 Å (r_s) in methyl formate.[40] The variation is probably not experimentally significant and we can take an average of 1·43 ± 0·01 Å. The most reliable determination of the *tr* C—O length in formic acid is 1·343 ± 0·010 Å (r_s),[41] and 1·334 ± 0·010 Å (r_s) has been reported for the similar bond in methyl formate.[40] Although some widely different values have been published for both formic and acetic acids, we feel that these are unreliable and that the correct distance is 1·34 ± 0·02 Å.

Carbon-fluorine bonds.[42] The r_s value for the *te* CF distance is 1·384 ± 0·001 Å in methyl fluoride.[1] The *tr* CF length is 1·347 ± 0·009 Å in vinyl fluoride[14] and 1·348 ± 0·015 Å in acetyl fluoride.[25] The distance in FC≡N and FC≡CH is in the range 1·26–1·28 Å.[43]

Carbon-chlorine bonds.[42] Accurate r_s values are available for methyl chloride[1] (1·781 ± 0·001 Å), vinyl chloride[13] (1·726 ± 0·002 Å) and cyanogen chloride[44] (1·631 ± 0·001 Å).

Carbon-silicon bonds. The bond length in mono-, di-, and tri-methyl silane[45] is 1·867 ± 0·002 Å (r_s), while that in vinyl silane[17] is 1·853 ± 0·003 Å (r_s). An r_s distance of 1·850 Å has been reported[46] for H_3SiCN.

The lengths of typical CX bonds, with X = N, O, F, Cl, and Si, are collected in the "Obs. r_{cx}" column of Table 2. The shortening of the *tr* and *di* bonds, relative to the bond to *te* carbon, is also listed. Now if the shortening observed for carbon-carbon single bonds is assumed to be due entirely to changes in the carbon hybridization, it is reasonable to transfer the reduction in carbon radius (0·025 Å for *tr* carbon and 0·067 Å for *di* carbon) to the CX bonds. The residual shortening of the CX bonds, after subtraction of this contribution from the carbon atom, is given in the last column of Table 2. A part of this residual shortening can be attributed to changes in hybridization of atom X; for example, the near-planar structure of formamide[35,36] and cyanamide[37] suggests that the nitrogen orbital contains a higher proportion of *s* character than in methylamine. However, it is difficult to ascribe the entire residual shortening (0·07–0·08 Å for CO and CN bonds) to hybridization changes, since the change from *te* to *tr* hybridization in carbon results in a shortening of only 0·025 Å. We therefore

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[35] R. J. Kurland and E. B. Wilson, *J. Chem. Phys.* 27, 585 (1957).

[36] C. C. Costain and J. M. Dowling, *J. Chem. Phys.* 32, 158 (1960).

[37] J. K. Tyler, I. F. Thomas, and J. Sheridan, *Proc. Chem. Soc.* 155 (1959); D. J. Millen, G. Topping, and D. R. Lide, to be published.

[38] P. Venkateswarlu and W. Gordy, *J. Chem. Phys.* 23, 1200 (1955).

[39] P. H. Kasai and R. J. Myers, *J. Chem. Phys.* 30, 1096 (1959).

[40] R. F. Curl, *J. Chem. Phys.* 30, 1529 (1959).

[41] G. H. Kwei and R. F. Curl, *J. Chem. Phys.* 32, 1592 (1960).

[42] We shall consider only molecules with a single halogen atom because of the well-known tendency toward shorter bonds when several halogens are attached to the same carbon.

[43] J. Sheridan and J. K. Tyler, *Nature, Lond.* 185, 96 (1960); *Proc. Chem. Soc.* 119 (1960).

[44] C. H. Townes, A. N. Holden, and F. R. Merritt, *Phys. Rev.* 74, 1113 (1948).

[45] L. Pierce and D. H. Petersen, *J. Chem. Phys.* 33, 907 (1960).

[46] Private communication from J. Sheridan; see also J. Sheridan and A. C. Turner, *Proc. Chem. Soc.* 21 (1960); N. Muller and R. C. Bracken, *J. Chem. Phys.* 32, 1577 (1960).

have a strong argument for bringing in electron delocalization as a major factor in the shortening of the CX bonds.

There is no contradiction in the conclusion that delocalization contributes significantly to the shortening of CN, CO, CF, and CCl bonds but has a negligible effect on CC bond lengths. The N, O, F, and Cl atoms have lone pairs of electrons, and it is reasonable to expect that the transfer of charge form these lone-pair orbitals into a conjugated system involving a double or triple bond would greatly increase the stability of the molecule. The situation is quite different when there are two multiple bonds, as in 1,3-butadiene, since the electrons which are involved in the delocalization must come from an already existing bond. Actually, there is other evidence to show that the amount of delocalization is much greater in molecules containing lone pairs adjacent to a multiple bond. For example, the barriers to internal rotation about the CO bond in formic acid and the CN bond in formamide are very much higher than the barriers found in hydrocarbons; furthermore, the nuclear quadrupole coupling constants in vinyl chloride indicate a significant deviation from axial symmetry in the CCl bond, while no such effect is found in ethyl chloride.

TABLE 2 CX BOND SHORTENING

X	C	Obs r_{CX} (Å)	Bond shortening[a]	Residual shortening[b]
N	*te*	1·47 ± 0·01		
	tr	1·36 ± 0·02	0·11	0·08 ± 0·03
	di	1·35 ± 0·02	0·12	0·05 ± 0·03
O	*te*	1·43 ± 0·01		
	tr	1·34 ± 0·02	0·09	0·07 ± 0·03
F	*te*	1·384 ± 0·001		
	tr	1·347 ± 0·01	0·037	0·01 ± 0·01
	di	1·27 ± 0·01	0·11	0·05 ± 0·01
Cl	*te*	1·781 ± 0·001		
	tr	1·726 ± 0·002	0·055	0·030 ± 0·003
	di	1·631 ± 0·001	0·150	0·083 ± 0·002
Si	*te*	1·867 ± 0·002		
	tr	1·853 ± 0·003	0·014	0·011 ± 0·005
	di	1·850	0·017	0·050

[a] Relative to *te* CX bond.
[b] After correction for change in carbon hydridization

It is interesting to note that the residual shortening of a CN bond is roughly the same for *tr* and *di* carbon. This is to be expected, since the NH_2 group provides only one lone pair to participate in the conjugated system. With halogen atoms, on the other hand, a much greater shortening occurs for *di* carbon, evidently because there are now two lone pairs to conjugate with the two π orbitals of the triple bond. In the case of silicon, where no lone pairs are available, there is a slight residual *lengthening* of the CSi bond, which indicates that delocalization is again a minor factor.

We have proposed a picture in which the length of a CC single bond is determined almost entirely by the hybridization of the carbon atoms, while electron delocalization effects have a strong influence on bond lengths in systems containing lone pairs. This appears to be the simplest scheme for explaining the observed bond-length variations, but no claim of uniqueness can be made. Some important factors have been omitted, such as the influence of an adjacent bond involving an atom of high electronegativity.[47] However, the comparisons have been made in such a way as to minimize these effects. It should be emphasized that these statements about the importance of electron delocalization refer only to its effect on bond length. It is fairly obvious that certain other molecular properties (e.g. dipole moments) are much more sensitive to conjugation and hyperconjugation.

BOND ANGLES AND HYBRIDIZATION

In the derivation of covalent radii for carbon only the simple hybridization types sp, sp^2, and sp^3 were considered, although intermediate degrees of hybridization are certainly possible. The only objective measure of hybridization which has been proposed is based on bond angles.[48] It is instructive to calculate the value of λ, in the expression $s + \lambda p$ for the hybrid wave function, from the observed bond angles in some of the molecules for which good r_s structures are available. Table 3 gives the results for the C–C single bond in several related molecules; λ_m refers to the orbital of the methyl carbon and λ_o to the other carbon atom involved in the bond. The value of the geometric mean $\sqrt{\lambda_m \lambda_o}$ is also given; this will equal 1·73 for a pure *te*--*te* bond and 1·56 for a pure *te*--*tr* bond. It is seen that the correlation between observed bond length and the value of $\sqrt{\lambda_m \lambda_o}$ is very poor—much poorer than we obtained by assuming the orbitals to be pure *te* or *tr*. Therefore, if we assert that hybridization has an important influence on the C–C bond length, we must conclude that bond angles do not provide a reliable measure of the hybridization.

TABLE 3. HYBRIDIZATION PARAMETERS FOR C–C BONDS

Molecule	λ_m	λ_o	$(\lambda_m \lambda_o)^{1/2}$	r_s (Å)
Propane	1·46	1·62	1·54	1·526 ± 0·002
Isobutane	1·74	1·66	1·70	1·525 ± 0·002
Propylene	1·52	1·38	1·45	1·501 ± 0·004
Acetaldehyde	1·58	1·36	1·46	1·500 ± 0·005
Acetyl fluoride	1·62	1·56	1·59	1·503 ± 0·003
Acetyl cyanide	1·64	1·48	1·56	1·490 ± 0·010

The difficulty of using bond angles in this way can also be illustrated by calculating the hybridization of the carbon orbital which makes up the σ component of the double bond in ethylene derivatives. Values of λ range from 1·03 in CH_2CHF and CH_2CF_2 to 1·31 in ethylene itself—i.e. about $\frac{3}{4}$ of the way from a pure sp to a pure sp^2 orbital. If λ were a true measure of the hybridization, we should expect a much greater variation in the double-bond distance than is actually found. Many other examples have been cited where bond angles give a misleading or impossible estimate of hybridization. We can only conclude that other factors are generally of greater importance in determining the angles.

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[47] I. Lindqvist, *Nova Acta Regiae Societatis Scientiarum Upsaliensis* (Ser. IV) Vol. 17, No. 11, Almqvist and Wiksells, Uppsala (1960).

[48] Ref. 32, pp. 194–196.