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THE VARIATION OF CARBON CARBON BOND LENGTHS WITH ENVIRONMENT AS DETERMINED BY SPECTROSCOPIC STUDIES OF SIMPLE POLYATOMIC MOLECULES

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Abstract A brief and critical review of the spectroscopic method of determining molecular structures is given The difficulties and present experimental accuracies of the method are discussed and comparisons with available diffraction values are made. Spectroscopic data on carbon–carbon bond lengths (accurate to 0·005 Å) which have been accumulated in recent years are summarized These show a simple dependence on bond environment, namely, that bond lengths increase linearly with an increase in the number of adjacent bonds

INTRODUCTION

RECENT developments in experimental techniques and in interpretation of experimental data have led to improved accuracy in the determination of molecular structure parameters by spectroscopic and diffraction studies. Thus at the present time bond lengths in simple molecules can be given to an accuracy of ±0·005 Å or better. This accuracy has made it meaningful to assemble values of bond lengths in related molecules and justifies an attempt to derive relationships between bond lengths and various other bond properties.

A dependence of the CC single bond length on environment was first recognized by Herzberg, Patat and Verleger[1] in 1937. From an analysis of the photographic infra-red spectrum of methylacetylene, they showed that the C—C bond length in methylacetylene was 1·460 Å as compared to 1·540 Å for the C—C bond length in ethane. Further evidence of the variation of the CC single bond length was reported in 1939 by Pauling, Springall and Palmer[2] from their electron diffraction investigations.

A dependence of the CC double bond length on environment was first shown by Overend and Thompson[3] in 1953 from their study of the infra-red spectrum of allene. They found a C=C bond length of 1·30 Å in allene as compared with 1·34 Å in ethylene.

In recent years abundant data based on infra-red, microwave and Raman spectra as well as on electron diffraction experiments have been accumulated which confirm the variation of CC bond lengths with environment.[4,5] An analysis of these data has led to an empirical relation[5] for this dependence, namely, that the C—C, C=C and C—H bond lengths increase linearly with increase in the number of adjacent bonds (or adjacent atoms).

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[1] G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.* **41**, 123 (1937).
[2] L. Pauling, H. D. Springall and K. J. Palmer, *J. Amer. Chem. Soc.* **61**, 927 (1939).
[3] J. Overend and H. W. Thompson, *J. Opt. Soc. Amer.* **43**, 1065 (1953).
[4] G. Herzberg and B. P. Stoicheff, Nature, *Lond.* **175**, 79 (1955).
[5] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).

It is the purpose of this paper to review very briefly the present status of experimental values of carbon–carbon bond lengths in simple polyatomic molecules. A summary is given of the most accurately known C - C, C=C and C≡C bond lengths determined from spectroscopic studies. An attempt is made to assess the deficiencies and accuracy of the spectroscopic method, and spectroscopic values of bond lengths are compared with available electron diffraction values. Finally, it is shown that the collected spectroscopic values confirm the simple relation, given above, of the dependence of carbon–carbon bond lengths on the number of adjacent bonds.

REVIEW OF THE SPECTROSCOPIC METHOD

In principle the spectroscopic method of determining molecular structures is simple and straightforward. From the molecular spectra (infra-red, microwave, Raman or electronic spectra) one obtains the rotational constants for a given vibrational state of the molecule under study. These are essentially reciprocals of the moments of inertia averaged over the vibrational state. When the rotational constants of a sufficient number of vibrational states are known it is possible to determine the constants for the equilibrium state (i.e. the minimum in the potential energy surface) and hence the equilibrium moments of inertia. The equilibrium structure can then be determined in two ways: (1) by solving a set of simultaneous equations of the moments of inertia for several isotopic species of the molecule,[*] the number of equations being equal to the number of unknown structural parameters,[6] or (2) alternatively, one can use the method described by Kraitchman[7] whereby the equilibrium position of each atom in a molecule is determined fromthe differences in the moments of inertia of two isotopic species of the molecule with the isotopic substitution being made for each atom in the molecule.[†] The two methods are entirely equivalent.

Following this brief discussion it may be well to emphasize several points about equilibrium structures. Firstly, molecular spectroscopy affords the only known means of determining equilibrium structures experimentally. Secondly, there is no ambiguity in the definition of equilibrium parameters and therefore the accuracy in evaluating these parameters is limited solely by experimental inaccuracies. With the best experimental techniques of today, equilibrium bond lengths can be given to $\pm 0{\cdot}001$ Å or better and bond angles to $\pm 15'$.

In practice, however, the experimental problems of obtaining such complete spectroscopic data for determining the equilibrium structures of polyatomic molecules are formidable. Up to the present time, the equilibrium structures of only the few polyatomic molecules listed in Table 1 have been reported.

On the other hand, spectroscopic data on the rotational constants for the ground vibrational states ($v_i = 0$) of molecules are more easily obtained, and values of these

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[*] For all diatomic molecules and for linear symmetric triatomic molecules as well as for some simple asymmetric top molecules (as for example those listed in Table 1) only the constants of one molecular species are necessary to determine the complete structure.

[†] Since one can use the first moment equations in addition to the moment of inertia equations, the number of isotopic substitutions can be reduced.[7] The minimum number of substitutions is n-2 for linear and planar asymmetric top molecules and n-3 for non-planar asymmetric top molecules, where n is the number of atoms in the molecule.

[6] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* pp. 395, 434, 487 Van Nostrand, Princeton (1945)

[7] J. Kraitchman, *Amer. J. Phys.* 21, 17 (1953)

constants are known for many polyatomic molecules. The ground state rotational constants give values of the "effective" moments of inertia or more precisely, they give average values of the reciprocals of the corresponding moments of inertia averaged over the zero-point vibrations.* It is the use of these "effective" moments of inertia that can lead to difficulties and sometimes to uncertainties in structure determinations.

The two methods for determining equilibrium structures, given above, can also be used for determining "effective" structures. In the first method one solves a set of simultaneous equations for the effective moments of inertia of several isotopic molecules and obtains the "effective" or "r_0" structure. However, a fundamental difference arises here: while it is expected that equilibrium internuclear distances (r_e) in isotopic molecules are the same (to better than ± 0·001 Å), it is known that effective internuclear distances (r_0) need not be exactly the same since the amplitudes of the zero-point vibrations are different in different isotopic molecules. The consequences of these "zero-point vibration effects" are well known.[6,8,9,10] One obtains slightly different "r_0" structures when solving equations for different sets of isotopic molecules,[8-10] the differences being largest when isotopic substitution has been made for an atom near a principal axis (within about 0·2 Å), or when the positions of hydrogen atoms are determined without deuterium substitution; also, ambiguities may arise because of the inertial defect for planar molecules[10] and because of analogous factors for non-planar molecules.[9]

Obviously we must discuss the question of just how much the "r_0" structures differ from the "r_e" structures. A comparison is made in Table 1 for all polyatomic molecules whose equilibrium structures are known. It is seen that the "r_0" values are no more than 0·005 Å larger than "r_e" and in most cases the differences are much less. (It may be mentioned here that this good agreement in "r_0" and "r_e" is found in all but a few of the known diatomic molecules. Of course, of necessity, one would not expect "r_0" and "r_e" to be the same in H_2, the lightest molecule, but even so they only differ by 0·009 Å.[11]) Unfortunately, only this limited comparison is possible at the present time for polyatomic molecules but the closeness of the "r_0" and "r_e" values shown here appears to confirm the belief of many spectroscopists that "r_0" structures are in fact very good approximations of the equilibrium structures.

Even better agreement with equilibrium structures is obtained by the second method of determining structures from ground state rotational constants. It is based on Kraitchman's equations[7] and the resulting effective structures are labelled "r_s" structures. Costain[10] has recently advocated this method and has given a detailed discussion of its advantages over the first method illustrated by several convincing examples. In this method one determines the co-ordinates (in the principal axis system) of each atom independently by making isotopic substitution for every atom in the molecule. In the calculations the differences of moments of inertia of two isotopic species are used and this results in a reduction of the zero-point vibration effects. It is found that the "r_s" structures are almost independent of the isotopic

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* Any ground state rotational constant (for example B_0) is defined as $B_0 = \frac{h}{8\pi^2 c}\left(\frac{1}{I_b^0}\right)_{av}$ see ref. 6, p. 461.

[8] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* p. 42. McGraw-Hill, New York (1955).

[9] V. W. Laurie, *J. Chem. Phys.* **28**, 704 (1958).

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

[11] B. P. Stoicheff, *Canad. J. Phys.* **35**, 730 (1957).

species used to determine the structures: that is, the consistency of the "r_s" structures determined from different sets of isotopic species is within ±0·001 Å.[10,12] Also, the errors in determing the co-ordinates of an atom are independent of the mass of the atom: therefore hydrogen atom positions are located with the same precision as positions of heavier atoms. As in the first method, errors may arise from the inertial defect or from substitution on atoms near a principal axis. In practice, the most reliable distances are those for atoms farther away than about 0·20 Å from principal axes. For atoms closer than 0·20 Å, the positions can be reliably determined by the use of the first moment equations if the positions of most of the other atoms have been determined: or when sufficient data are available, namely moments of inertia of doubly substituted atoms, one can use the second differences of the moments for locating "near-axis" atoms.[13] Other advantages are that partial structures may be determined by making isotopic substitutions only on atoms whose positions are required and that probable errors can be given for the co-ordinates of each atom. At present, isotopic substitution at each atom is not always feasible. In spite of this difficulty it is possible to determine "r_s" structures by microwave spectroscopy since its high sensitivity and high resolution permits the study of many isotopic molecules in their natural abundances. In infra-red and Raman spectroscopy, however, isotopic substitution is almost solely restricted to replacement of hydrogen by deuterium. A comparison of "r_s" and "r_e" structures is made in Table 1. It is seen that the "r_s" values are within ±0·003 Å of the equilibrium values.

In conclusion, the present status of the spectroscopic method of determining molecular structures may be summarized as follows. The equilibrium structures of less than ten polyatomic molecules are known. Unfortunately, progress in this important field is slow and for a long time to come we shall have to be content with structure parameters obtained from ground state rotational constants. While the difficulties and limitations of such structure determinations are recognized there is considerable reason for optimism with the "r_s" and "r_0" structure parameters. The available data (Table 1) show that these parameters are the same as equilibrium parameters within 0·005 Å for bond lengths and 1° for bond angles, the "r_s" values being somewhat better than the "r_0" values. It is this closeness of "r_s" and "r_0" values to "r_e" values which now makes worthwhile the collection of bond lengths in related molecules in order to look for possible relations with bond properties.

COMPARISON OF SPECTROSCOPIC AND DIFFRACTION STRUCTURAL PARAMETERS

While the present paper is intended to deal primarily with spectroscopic structure determinations it is of interest to compare briefly the available diffraction and spectroscopic data. Such comparisons may be of importance in establishing possible differences in apparent structures determined by these two experimental methods. In Table 2 are listed the diffraction and spectroscopic values of structural parameters in several simple molecules. Only those values are included which were considered by the original investigators to be accurate to ±0·005 Å and ±1°. Also, the results of as many investigators as possible are included in order to test the reproducibility of structure determinations.

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

[12] L. Pierce, *J. Mol. Spectroscopy* 3, 575 (1959); L. C. Krisher and L. Pierce, *J. Chem. Phys.* 32, 1619 (1960)

It is seen that most of the values agree to within the experimental accuracy quoted above. Such good general agreement amongst the several different experimental techniques and amongst the various authors using the same technique is encouraging. Yet there are some significant differences which bear closer examination. For example, the diffraction values of the CH bond lengths in CH_4 (and CD_4) as well as in CH_3Cl are between 0·010 Å and 0·020 Å larger than the corresponding spectroscopic values and there is a discrepancy of about 2° in the values of the HCH angle in C_2H_4. These differences are several times the experimental errors given by the original investigators and appear to support the suggestion that there may be significant differences in the results of spectroscopic and diffraction structure determinations. Such differences may become more apparent as the accuracy of both techniques is improved and would be more conclusive if electron diffraction data for diatomic molecules were available for comparison with existing spectroscopic data. According to the results in Table 2, there appear to be small differences amongst different experimenters using the same methods, for example in the spectroscopic values obtained for the C–C bond length in ethane, and in the diffraction values of the C–C bond length in n-butane. Differences of this kind can only mean that further efforts are necessary by all investigators to adequately assess and to improve the accuracy of experimental values.

In spite of the generally good agreement shown in Table 2 between the diffraction and spectroscopic values of molecular structures, the main conclusions of this paper are based on spectroscopic results, not only because they are more plentiful but also for the sake of consistency. For the sake of completeness, however, the available electron diffraction values are included in the present compilation.

SUMMARY OF CARBON-CARBON BOND LENGTHS IN SIMPLE POLYATOMIC MOLECULES

The most extensive collection of CC bond lengths covering the period up to 1955 was published by Sutton *et al.*[14] in 1958. This collection includes all the CC bond lengths believed to be known to ±0·02 Å or better. Shorter compilations of values known more accurately have also been given;[4,5,15] one of these[5] includes only those values believed to be accurate to ±0·005 Å or better. The present collection of bond lengths forms an extension to the latter paper.

Tables 3 and 4 contain the CC bond lengths of all the gaseous polyatomic molecules for which accurate data are available. Table 3 includes open chain molecules and Table 4 cyclic molecules. The quoted bond lengths are considered to be the best values available at the present time. Most of the values are reported to be accurate to at least ±0·005 Å. A few values which are less accurate (to only ±0·01 Å) either because of larger experimental error or because they are not independent of some assumptions, have been included and are correspondingly labelled. As mentioned in the preceding section, most of the data have been obtained from molecular spectra, mainly from microwave spectra. The values are all "r_s" or "r_0" parameters determined from ground state rotational constants. Electron diffraction values (also reported to be accurate to ±0·005 Å or better) are included in Tables 3 and 4 to

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[14] L. E. Sutton, D. G. Jenkin, A. D. Mitchell, L. C. Cross, H. J. M. Bowen, J. Donohue, O. Kennard, P. J. Wheatley and D. H. Whiffen, *Tables of Interatomic Distances and Configuration in Molecules and Ions* The Chemical Society, London (1958)

[15] M. G. Brown, *Trans. Faraday Soc.* 55, 694 (1959)

indicate their trend with changes in bond environment. A summary of CH bond lengths in simple polyatomic molecules is given in ref. 5.

DEPENDENCE OF CC BOND LENGTHS ON ENVIRONMENT

An examination of the bond lengths given in Table 3 confirms the conclusions of several recent investigations, namely, that the bond lengths for a given bond environment are remarkably constant in different molecules. This appears to be true even in the few examples where atoms of very different electronegativities are adjacent to the CC bonds. For the C—C bond length, a small change is indicated when Cl, Br and F atoms are adjacent to the bond. But the scarcity of such data does not allow any conclusions to be drawn, at present, on the dependence of CC bond lengths on different adjacent atoms. The bond length data on ring compounds (Table 4) are also scanty and little can be said concerning a dependence on environment.

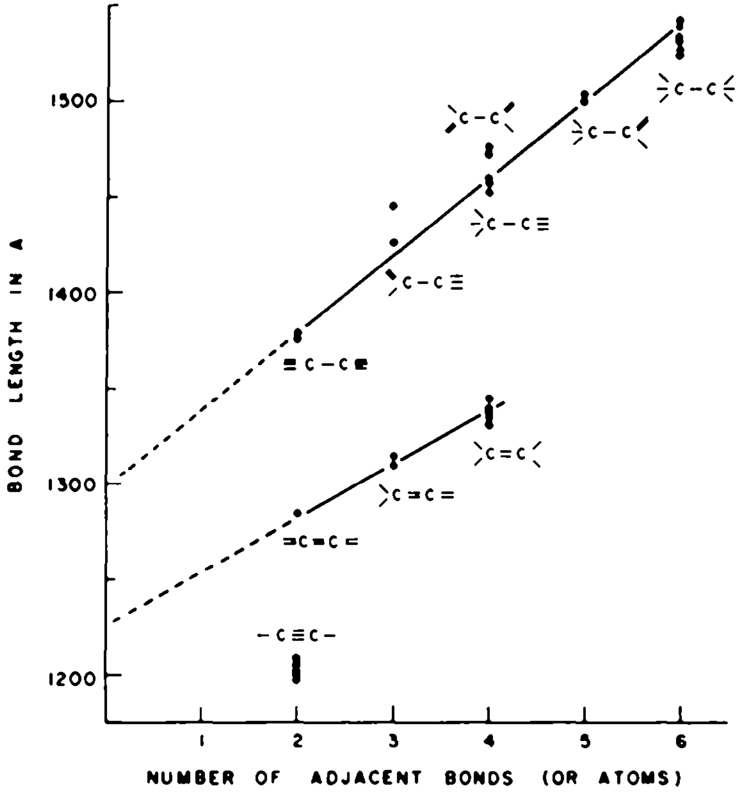

FIG. 1

The data on C—C and C=C bond lengths confirm the earlier conclusions[4,5] that the bond lengths change systematically with the changes in bond environment: specifically, the bond lengths increase linearly with increase in the number of adjacent bonds (or adjacent atoms). These relationships are shown in the graphs of Fig. 1. Most of the values for the C—C bond lie within $\pm 0{\cdot}005$ Å of a straight line given by the equation

$$r(\mathrm{C—C}) = 1{\cdot}299 + 0{\cdot}040\,n \qquad n = 2, 3 \ldots 6$$

(where n is the number of adjacent bonds).

All the values for the C=C bond lie close to another straight line given by the equation

$$r(\mathrm{C{=}C}) = 1{\cdot}226 + 0{\cdot}028\,n \qquad n = 2, 3, 4$$

Thus an analysis of the available spectroscopic data has given empirical relations for the average or "normal" behaviour of C—C and C=C (as well as C—H)[5] bond lengths.

There appear to be a few exceptions to this behaviour for the C—C bond. These include the values for butadiene, acrolein and propynal, the latter two being "r_s" values. The value given for butadiene is an "r_0" value but unfortunately is based on assumed ethylene parameters for the two CH—$\mathrm{CH_2}$ groups. There is also, apparently, a rather wide range of values for the $-\mathrm{C}-\overset{/}{\underset{/\ \ \backslash}{\mathrm{C}}}-$ bond length: these may be grouped into three values, 1·539 Å (r_0, ethane), 1·533 Å (r_s, ethyl fluoride) and 1·526 Å (r_s, propane, isobutane). The discrepancy between the ethane and propane-isobutane values appears to be too large to be accounted for by a difference in "r_s" and "r_0" values: one might perhaps expect a difference of at most 0·005 Å and hence an "r_s" ethane value of about 1·534 Å. A closer look at the isobutane structure determination shows that the off-axis C atoms are only 0·10 Å from the x-y plane (determined by $\mathrm{C^{13}}$ substitution) and their positions are subject to appreciable error, perhaps in the range of 0·010 to 0·020 Å. It is known that the "r_s" method errs in giving an apparent co-ordinate which is too small for "near-axis" atoms and thus it is possible that the C—C bond length in isobutane may be as large as 1·532 Å. The short C—C bond in propane is reminiscent of the short CH bond in methane,[5] the latter being approximately 0·01 Å shorter than the CH bonds in ethane, methyl acetylene and methyl cyanide.

No attempt has been made in this paper to explain the dependence of CC bonds on environment. Other authors have attempted to explain this dependence in terms of various descriptions of the carbon atoms and their environment. For example: Somayajulu[17] and notably Brown[15] and Dewar and Schmeising[16] discuss this dependence predominantly in terms of hybridization: Bernstein[18] in terms of π-bond orders; Mulliken[19] in terms of hybridization with appreciable contribution form conjugation and hyperconjugation; Bak and Nygaard[20] in terms of hybridization and electron delocalization; Wilmshurst[21] in terms of hybridization, bond order and ionicity; and Bartell[22] in terms of van der Waal's interactions between non-bonded atoms.

It is very difficult to test the validity or to determine the relative importance of these various concepts. This has not been the purpose of the present paper. Rather, the aim has been to establish experimentally the existence of a dependence of CC bond lengths on their environment.

I am grateful to Dr. G. HERZBERG and Dr. C. C. COSTAIN for many helpful discussions on this subject.

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[16] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* 5, 166 (1959); 11, 96 (1960).

[17] G. R. Somayajulu, *J. Chem. Phys.* 31, 919 (1959).

[18] H. J. Bernstein, *J. Phys. Chem.* 63, 565 (1959).

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

[20] B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.* 33, 418 (1960).

[21] J. K. Wilmshurst, *J. Chem. Phys.* 33, 813 (1960).

[22] L. S. Bartell, *J. Amer. Chem. Soc.* 81, 3497 (1959).

TABLE 1. COMPARISON OF EQUILIBRIUM AND GROUND STATE MOLECULAR STRUCTURES DETERMINED EXPERIMENTALLY BY SPECTROSCOPIC METHODS

Molecule	Parameters	r_e[a]	r_0	r_s	Ref
CO_2	r(CO)	1·1600	1·162	1·1607	23
CS_2	r(CS)	1·5531	1·555	1·5525	24
HCN	r(CH)	1·0630	1·064	1·0632	10, 25
	r(CN)	1·1538	1·156	1·1554	
N_2O	r(NN)	1·126	1·129	1·1286	10
	r(NO)	1·186	1·191	1·1876	
H_2O	r(OH)	0·9572	0·963[b]	0·9609[b]	26
	∠(HOH)	104°31′	104°2′	103°33′	
D_2O	r(OD)	0·9575	0·962[b]	0·9615[b]	26
	∠(DOD)	104°29′	104°7′	104°21′	
NH_3	r(NH)	1·0124	1·017	1·0139[c]	27
	∠(HNH)	106°41′	107°47′	107°20′[c]	
ND_3	r(ND)	1·0108	1·016		27
	∠(DND)	106°42′	107°36′		
C_2H_2	r(CH)	1·0585	1·061		28, 29
	r(CC)	1·2047	1·207		

[a] All bond lengths are given in Å units.

[b] Average values obtained by taking I_A, I_B, I_C in pairs. If only I_A and I_B are used in the calculations the r_0 and r_s values are within 0·002 Å from the equilibrium values.

[c] The NH_3 and ND_3 values are necessary to obtain the "r_s" parameters.

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[23] C. P. Courtoy, *Ann. Soc. Sci. Bruxelles* 73, 5 (1959).

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[25] J. W. Simmons, W. E. Anderson and W. Gordy, *Phys. Rev.* **86**, 1055 (1952).

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[28] M. T. Christensen, D. R. Eaton, B. A. Green and H. W. Thompson, *Proc. Roy. Soc.* A **238**, 15 (1956).

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

TABLE 2. COMPARISON OF GROUND STATE MOLECULAR STRUCTURES DETERMINED EXPERIMENTALLY BY DIFFRACTION AND SPECTROSCOPIC METHODS

Molecule	Parameter	Diffraction value[a]	Spectroscopic value[b]
NH_3	r(NH)	$1·016^{30c}$	$1·0173$ I^{27}
ND_3	r(ND)	$1·017^{30}$	$1·0155$ I^{27}
CH_4	r(CH)	$1·107_0{}^{31}$	$1·0940$ R^{32} $1·0941$ I^{33}
CD_4	r(CD)	$1·102_1{}^{31}$	$1·092_3$ R^{34}
C_2H_4	r(CH)	$1·084^{35}$	$1·086$ I^{36} $1·086$ R^{37}
	r(CC)	$1·332_1$	$1·337$ $1·339$
	∠(HCH)	115°30′	117°22′ 117°34′
CH_3Cl	r(CH)	$1·114^{38}$	$1·096$ M^{19}
	r(CCl)	$1·783$	$1·7812$
C_2H_6	r(CH)	$1·107^{39}$	$1·102$ I^{40}
	r(CC)	$1·536$	$1·543$ $1·534$ I^{41} $1·538$ R^{42}
C_3H_4	r(CC)	$1·312^{43}$	$1·309$ R^{44}
(Allene)	r(CH)	$1·082$	$1·080$ I^{45}
C_6H_6	r(CC)	$1·393^{46}$ $1·39_2{}^{47}$ $1·397^{48}$	$1·397$ R^{49}
	r(CH)	$1·083$	$1·084$
C_4H_{10}	r(CC)	$1·533^{50}$ $1·540^{51}$	
(n-butane)	r(CH)	$1·108$ $1·100$	

[a] All values have been obtained by electron diffraction experiments with gaseous molecules, the only exception being the CC bond length in benzene which was obtained by x-ray diffraction experiments with benzene crystals.

[b] The spectroscopic values have been obtained by means of infra-red (I) Raman (R) and microwave (M) spectra of gaseous molecules.

[c] The superscripts are reference numbers

[30] A. Almenningen and O. Bastiansen, *Res. Correspondence* 9, 35 (1956).
[31] L. S. Bartell, K. Kuchitsu and R. J. de Neui, *J. Chem. Phys.* 33, 1254 (1960).
[32] M. A. Thomas and H. L. Welsh, *Canad. J. Phys.* 38, 1291 (1960).
[33] K. T. Hecht, J. Mol. *Spectroscopy* 5, 390 (1960).
[34] G. G. Shepherd and H. L. Welsh, *J. Mol. Spectroscopy* 1, 277 (1957).
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[36] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.* **80**, 2673 (1958).
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[38] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.* 23, 1860 (1955).
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[40] G. E. Hansen and D. M. Dennison, *J. Chem. Phys.* **20**, 313 (1952).
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[42] B. P. Stoicheff, *Canad. J. Phys.* to be published.
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[47] E. G. Cox, D. W. J. Cruickshank and J. A. S. Smith, *Proc. Roy. Soc.* A **247**, 1 (1958).
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[49] A. Langseth and B. P. Stoicheff, *Canad. J. Phys.* **34**, 350 (1956).
[50] R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.* **81**, 3491 (1959).
[51] K. Kuchitsu, *Bull. Chem. Soc. Japan* **32**, 748 (1959).

TABLE 3 A SUMMARY OF CC BOND LENGTHS IN OPEN CHAIN MOLECULES

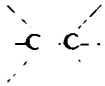
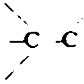
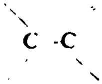
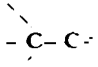
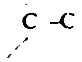
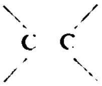
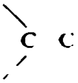
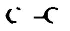
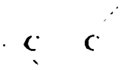
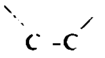
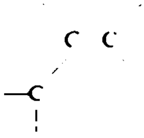
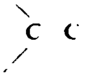
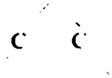
Bond type	Length^a	Molecule	Reference^b
	1.543	ethane C_2H_6	I, 40
	1.538	ethane C_2H_6	R, 42
	1.534	ethane C_2H_6	I, 41
	1.533	ethyl fluoride CH_3CH_2F	M, 52
	1.526	propane $CH_3CH_2CH_3$	M, 53
	1.525	isobutane $(CH_3)_3CH$	M, 54
	1.540	n-butane C_4H_{10}	ED, 51
	1.536	ethane C_2H_6	ED, 39
	1.534	n-heptane C_7H_{16}	ED, 55
	1.533	n-hexane C_6H_{14}	ED, 55
	1.533	n-butane C_4H_{10}	ED, 50
	1.531	n-pentane C_5H_{12}	ED, 55
	1.503	acetyl fluoride CH_3CFO	M, 56
	1.501	propylene CH_3CHCH_2	M, 57
	1.501	acetaldehyde CH_3CHO	M, 58
	1.505	isobutylene $(CH_3)_2CCH_2$	ED, 59
	1.476 ± 0.01	butadiene $CH_2(CH)_2CH_2$	R, I, 60
	1.472	acrolein CH_2CHCHO	M, 61
	1.483 ± 0.01	butadiene	ED, 62
	1.459	methylacetylene CH_3CCH	M, 10
	1.458	methylbromoacetylene CH_3CCBr	M, 63
	1.458	methyl cyanide CH_3CCN	M, 10
	1.458	methylchloroacetylene CH_3CCCl	M, 64
	1.454	methylcyanoacetylene CH_3CCCN	M, 65
	1.445	propynal CHCCHO	M, 12
	1.426	vinyl cyanide CH_2CHCN	M, 5
	1.378	cyanoacetylene HCCCN	M, 10
	1.375	methylcyanoacetylene CH_3CCCN	M, 65
	1.344	acrolein CH_2CHCHO	M, 61
	1.339	ethylene C_2H_4	R, 37
	1.339	vinyl cyanide CH_2CHCN	M, 5
	1.337	ethylene C_2H_4	I, 36
	1.336	propylene CH_3CHCH_2	M, 57
	1.332	vinyl chloride CH_2CHCl	M, 66
	1.337	butadiene $CH_2(CH)_2CH_2$	ED, 62
	1.333	ethylene C_2H_4	ED, 35
	1.331	isobutylene $(CH_3)_2CCH_2$	ED, 59
	1.314	ketene CH_2CO	M, 67
	1.309	allene CH_2CCH_2	R, 44
	1.312	allene CH_2CCH_2	ED, 43
	1.284	butatriene CH_2CCCH_2	R, 68
	1.280 ± 0.01	carbon suboxide C_3O_2	ED, 69, 70
	1.209	propynal CHCCHO	M, 12
	1.207	acetylene C_2H_2	I, R, 28, 29
	1.205	methylacetylene CH_3CCH	M, 10
	1.205	cyanoacetylene HCCCN	M, 10
	1.205	methylcyanoacetylene CH_3CCCN	M, 65
	1.204	chloroacetylene CHCCl	M, 63
	1.201	methylbromoacetylene CH_3CCBr	M, 63
	1.198	fluoroacetylene CHCF	M, 71

TABLE 4 A SUMMARY OF CC BOND LENGTHS IN CYCLIC MOLECULES

Bond type	Length[a]	Molecule	Reference[b]
	1.549	trimethylene oxide C_3H_6O	M, 72
	1.558	cyclobutane C_4H_8	R, 73
	1.515	cyclopropene $CH_2(CH)_2$	M, 74
	1.423	thiophene C_4H_4S	M, 76
	1.462	cyclooctatetraene C_8H_8	ED, 75
	1.397	benzene C_6H_6	R, 49
	1.394	pyridine C_5H_5N	M, 77
	1.397	benzene C_6H_6	ED, 48
	1.393	benzene C_6H_6	ED, 46
	1.370	thiophene C_4H_4S	M, 76
	1.300	cyclopropene $CH_2(CH)_2$	M, 74

Footnotes for Table 3 and 4

[a] All bond lengths are in Å units (i.e. 10^{-8} cm)

[b] M – microwave, R – Raman, I – infra-red, ED – electron diffraction.

[c] In order to obtain these values some of the structural parameters were assumed.

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