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THE NATURE OF BONDS BETWEEN CARBON ATOMS HOW THEY VARY WITH ENVIRONMENT

O. BASTIANSEN and M. TRÆTTEBERG
Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

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INTRODUCTION

As a result of the incapability of quantum mechanics to yield an accurate and decisive solution for a system with a given number of nuclei and electrons, the whole theory of the chemical bond is based upon approximation calculations. These calculations have to a great extent been guided by experimental results, of which bond-length measurements and conformation studies have been of particular importance. The approximation approach has led to the introduction of a series of concepts that have often been introduced as a result of mathematical resignation. These concepts are therefore often merely of formal value and accordingly not of an obvious physical nature, though they are often referred to as "effects". Among these concepts some of the most important ones are hybridization, electron delocalization, resonance, conjugation, hyperconjugation, electronegativity, and steric effects.

Perhaps the most important characteristic of the chemical bond is the bond length. For the carbon–carbon bond the bond length does not vary much with the environment. It is often the case that a change in bond environment will lead to a bond distance effect which is less than the error limits of the experimental methods in use for bond length measurement. For the development of the theory of the chemical bond it is therefore of great importance to improve the experimental technique. It is also important to understand the principal differences of the results obtainable from the various methods. The safest procedure is to compare distances obtained using always the same experimental method.

The present contribution is nearly exclusively based upon results obtained by the Norwegian electron-diffraction group. It should be emphasized that all the molecules are studied in the vapour phase. The present authors would consider it too ambitious to try to cover more of the field than the very limited results of their own school. The field as a whole will no doubt be taken care of by the other contributors to this papers symposium.

Even when comparing results obtained from the same experimental method great difficulties arise as to the accuracy of the bond distance determinations. In the case of the electron-diffraction method for instance, the accuracy may be different for different compounds and also for different bonds in the same molecule. It is, therefore, very difficult to give a definite statement as to the accuracy. In favourable cases a bond distance can be reproduced to an accuracy of 0·001 Å. Reproducibility is, however, not the same thing as the absolute accuracy that depends upon scale factors and complicated definitions as to what a bond length actually means.

TABLE 1. C—C BOND DISTANCES OBTAINED FROM SPECTROSCOPIC METHODS AND FROM ELECTRON-DIFFRACTION

Type of bond	Bond distances in Å spectroscopic	Bond distances in Å electron diffraction
C C	1·534[1]	1·536 ethane[2]
C- C	1·501[3]	
C–C	1·485[4]	1·483 1,3-butadiene[5] 1·462 cyclo-octatetraene[6]
C –C	1·459	1·450 dimethyldiacetylene[7]
C–C	1·426[8]	1·425 vinylacetylene[9]
C -C	1·377[10, 11]	1·377 dimethyldiacetylene[7]
C C	1·338	1·337 1,3—butadiene[5] 1·334 cyclo-octatetraene[6] 1·336 vinylacetylene[9]
C-C	1·311[12-14]	1·312 allene[15] 1·318 butatriene[16]
C C	1·284[17]	1·283 butatriene[16]
C- C	1·207	1·207 vinylacetylene[9] 1·208 dimethyldiacetylene[7]

COVALENT RADII FOR CARBON

A number of hydrocarbons have been studied by the Norwegian electron-diffraction group. In Table 1 a series of C- C bond distances of non-aromatic open chain molecules have been listed and compared with distances obtained by spectroscopic methods. Some of the spectroscopic values are average values from several investigators. The general correspondence between the spectroscopically obtained values and the electron-diffraction values is satisfactory. The bonds have been grouped into

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[1] H. C. Allen and L. K. Plyler, *J. Amer. Chem. Soc.* **31**, 1062 (1959).
[2] A. Almenningen and O. Bastiansen, *Acta Chem. Scand.* **9**, 815 (1955).
[3] R. W. Kilb, C. C. Lin and E. B. Wilson, Jr., *J. Chem. Phys.* **26**, 1695 (1957).
[4] B. P. Stoicheff, Private communication (1959).
[5] A. Almenningen, O. Bastiansen and M. Trætteberg, *Acta Chem. Scand.* **12**, 1221 (1958).
[6] O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.* **27**, 1311 (1957).
[7] A. Almenningen, O. Bastiansen and T. Munthe-Kaas, *Acta Chem. Scand.* **10**, 261 (1956).
[8] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).
[9] T. Munthe-Kaas, Thesis, Oslo University (1955).
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[12] A. A. Westenberg and E. B. Wilson, Jr. *J. Amer. Chem. Soc.* **72**, 199 (1950).
[13] H. R. Johnson and M. W. P. Strandberg, *J. Chem. Phys.* **20**, 687 (1952).
[14] B. P. Stoicheff, *Canad. J. Phys.* **33**, 811 (1955).
[15] A. Almenningen, O. Bastiansen and M. Trætteberg, *Acta Chem. Scand.* **13**, 1699 (1959).
[16] A. Almenningen, O. Bastiansen and M. Trætteberg (unpublished).
[17] B. P. Stoicheff, *Canad. J. Phys.* **35**, 837 (1957).

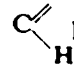
the usual ten categories defined by the hybridization, six for the single bond, three for the double bond, and one for the triple bond. It seems to be of great importance to the theory of the C—C bond to extend this table to a larger number of molecules. An extended table would give valuable informations as to the relative importance of hybridization and bond delocalization. Without entering into the controversies on this point we shall make some comments from our data: The electron-diffraction bond lengths given in Table 1 form bases for calculating covalent radii for the carbon atom applicable for C—C bonds. The radii are given in Table 2. Of course the number of compounds presented in Table 1 is not sufficient to draw any far-reaching conclusion. On the other hand the given radii and a series of similar radii values published by other authors[8,18–20] indicate the usefulness of the kind of arguments leading to these values.

TABLE 2 COVALENT RADII OF THE C-ATOM FOR DIFFERENT TYPES OF HYBRIDIZATION

Bond multiplicity	$C-$	$C=$	$C\equiv$
sp^3	0·767		
sp^2	0·737	0·669	
sp	0·687	0·642	0·604

If one desires to argue in terms of σ-bonds and localized π-bonds some simple conclusions may be drawn. The bond shortening effect of a π-bond can for instance be studied. Comparing the three combinations sp^2sp^2, sp^2sp, and $spsp$, the bond shortening effect going from a single bond to the corresponding double bond is 0·137, 0·110 and 0·094 Å respectively. It is reasonable that the effect decreases with the length of the single bond to be contracted. In a similar way the effect of the first and second π-bond in an $spsp$ bond could be studied. The first π-bond contracts the total bond by an amount of 0·094 Å. The effect of the second bond is 0·076 Å. In Fig. 1 the bond shortening caused by one π-bond has been given as a function of the uncontracted distance. In this presentation the effect of the π-bond delocalization has of course been neglected, and this effect should according to the usual resonance theory be expected to be rather large.

THE sp^2-sp^2 C—C SINGLE BOND

For the study of resonance effects in terms of π-bond electron delocalization, the sp^2-sp^2 single bond is of particular interest. Two examples of such a bond are given in Table 1, namely for cyclo-octatetraene and for 1,3-butadiene. The bond distance is found to be 0·021 Å larger for 1,3-butadiene than for cyclo-octatetraene. This is a remarkable result in view of the fact that the 1,3-butadiene molecule is found to be a planar *trans* molecule while the bond arrangement around the single bond in cyclo-octatetraene is far from planar, the angle between the two -  planes being approximately 60°. This finding, if real, seems to be an important argument in the

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discussion of the influence of conjugation on the C–C single bond length. One must seek for arguments to explain the difference in the two distances as well as the fact that the 1,3-butadiene molecule is planar. If resonance does not result in a shortening of the central C–C bond distance, how could it then possibly be responsible for the planarity? A natural argument might be sought in the interaction between hydrogen atoms. One might for instance expect the hydrogen-hydrogen distances in the planar 1,3-butadiene molecule to be particularly favourable. However, a recent calculation carried out by Fischer-Hjalmars[21] does not seem to support this argument. According to her calculations, conjugation energy plays a more important part than the hydrogen-hydrogen interaction. If the dilemma is to be explained by resonance, the effect may perhaps be related to the cyclic form of cyclo-octatetraene that might favour the *p*-electron delocalization. One could of course question the reality of the effect. Though there are all reasons to believe that the effect is real, the authors feel in view of the importance of the problem that a simultaneous reinvestigation of cyclo-octatetraene and 1,3-butadiene should be carried through.

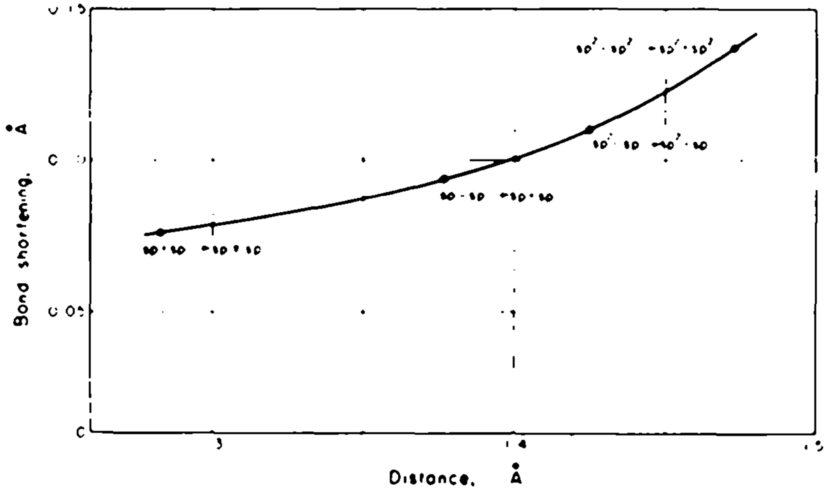

FIG. 1 Bond shortening caused by one π-bond as a function of the distance. (Values from the Norwegian electron diffraction work.)

The sp^2-sp^2 single bond has been studied by the electron-diffraction method in a whole series of molecules where two aromatic rings are linked together. These molecules are, for example, biphenyl[22] and its derivatives,[23,24] bipyridyls,[22] sym-triphenylbenzene,[25] hexaphenylbenzene,[26] and 2,2′-dithienyl.[27] Unfortunately the bridge C—C bond distance in these molecules cannot be determined with particularly great accuracy by electron diffraction. The relative contribution of the bridge bond to the total electron scattering is small, and the distance has to be determined indirectly by studying larger internuclear distances between two different rings. Biphenyl itself is probably that of the above molecules for which the most accurate

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[21] I. Fischer-Hjalmars, to be published.

[22] A. Almenningen and O. Bastiansen, *Kgl. Norske Vid. Selsk. Skr.* No. 4 (1958).

[23] O. Bastiansen, *Acta Chem. Scand.* 4, 926 (1950).

[24] O. Bastiansen and L. Smedvik, *Acta Chem. Scand.* 8, 1593 (1954).

[25] O. Bastiansen, *Acta Chem. Scand.* 6, 205 (1952).

[26] A. Almenningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.* 12, 1215 (1958).

[27] A. Almenningen, O. Bastiansen and P. Svendsås, *Acta Chem. Scand.* 12, 1671 (1958).

distance value has been obtained. It was found to be 1·489 Å with a standard deviation of 0·0075 Å. The molecule seems to be far from rigid, and a rather large amplitude of rotational oscillation around the equilibrium position seems to exist. However, the electron-diffraction studies give a clear indication for a non-planar equilibrium conformation with an angle of 41·6° between the two phenyl rings. The deviation from planarity in the gaseous phase can easily be explained by interaction between hydrogen atoms. A comparison between the results of 1,3-butadiene and that of biphenyl also favours the idea that resonance seems to play a less important part for the bond distance. The two sp^2-sp^2 C—C distances are, within the error of the method, the same in spite of the less favourable angle arrangement for biphenyl.

For the other molecules containing aromatic rings linked together with single bonds the electron-diffraction studies carried out so far hardly give sufficiently accurate values for the bridge bond length to draw decisive conclusions. Altogether about 15 such molecules have been studied with results ranging from 1·47 to 1·52 Å. Some of these results have been obtained using older technique and are therefore less reliable. The only result beside biphenyl that might be accurate enough to be considered in this relation is that from hexaphenylbenzene. The sp^2-sp^2 C—C bond length was found to be 1·515 Å.[20] The estimated error limit is 0·015 Å. If this deviation from the biphenyl values is real, the longer distance might reasonably be related to the average 90° angle found between two directly linked rings.[21] The 1·515 Å distance should then correspond to an sp^2-sp^2 distance free of p-electron delocalization effects. Steric effects are of course of great importance for the conformation of the molecule, as interaction between hydrogen atoms no doubt is responsible for the 90° angle between each of the peripherical rings and the central ring. But also in the orthogonal conformation there are steric difficulties due to interaction between carbon atoms in neighbouring peripherical rings. This steric effect is, however, probably too small to contribute appreciably to the lengthening of the C—C bridge bond.

A systematic study of the angle between neighbouring rings in the biphenyl and bipyridyl group of molecules may throw some light on the resonance effect. For biphenyl and 4,4′-bipyridyl the deviation from planarity in the gaseous state is found to be as large as 42° and 37° respectively.[22] The resonance energy that should be gained in the planar form does not seem to be sufficient to overcome the repulsion between hydrogen atoms. A molecule of considerable interest in this connection is the 2,2′-bipyridyl molecule. In the *trans* form this molecule should be free from steric difficulties. One should, therefore, expect to find a pure *trans* molecule. This is not the case. The molecule does not seem to exhibit any well defined conformation. There seems to be a nearly free rotation through large angle intervals. The resonance energy does not seem to be large enough to keep the 2,2′-bipyridyl molecule in the sterically unhindered planar *trans* form. One might ask for the effect of the attractive force between the two hydrogen atoms in *ortho* position to the bridge bond. If this force were predominating, the molecule would have assumed an unplanar *cis* form corresponding to the most favourable H—H van der Waals' distance. Probably both the *trans* form and this unplanar *cis* form may correspond to energy minima, but the maxima in the energy curve given as a function of the angle, does not seem to be sufficiently high to favour any of the two stable conformations at the temperatures applied in the electron-diffraction experiment.

A group of molecules of interest in this connexion are the 2,2′-dihalobiphenyls.

Electron-diffraction studies lead to the surprising result that these molecules prefer a near *cis* instead of a near *trans* conformation. The inter planar angles found are 60°, 74°, 75° and 79° for the fluoro-, chloro-, bromo- and iodo-derivatives respectively. (Angle zero refers to the planar *cis* form.)[23,24] The conclusion to be drawn is that attractive van der Waals' forces of the London force type and not the repulsive dipole forces play the predominating part for these molecules. Conclusions along the same lines were obtained by Hampson and Weissberger from their dipole moment measurements.[25]

INFLUENCE OF NEGATIVE GROUPS

Of particular interest for our understanding of the influence of environment on the carbon–carbon bond are studies of molecules containing halogen atoms or other negative groups in the neighbouring position to the bond in question. Unfortunately the literature describing bond length measurements does not seem to form the basis for empirical rules. The present authors have made a list of approximately 50 molecules from the literature of the last few years without being able to discover any real systematical trends. There are many examples indicating bond length effects due to negative neighbour atoms but the results are often contradictory. For example, in hexafluoroethane indications are found for a somewhat larger C—C bond length than in ethane.[29] On the other hand recent work by Morino and Hirota[30] for hexachloroethane leads to a C—C bond distance considerably shorter than that of ethane. In the case of ethylene derivatives Morino *et al.*[31] have found a C—C bond distance in tetrafluoro- and 1,1'-difluoroethylene somewhat shorter than the ethylene distance, while microwave and infra-red work by Dowling[32] for 1,1'-dibromoethylene lead to a distance slightly larger than that of ethylene. It seems to be very difficult to find a single theory that can explain the various shortenings and lengthenings observed. The feeling of the present authors is that considerably more systematic experimental work should be carried out in this field before theoretical explanations are aimed at. It might be mentioned that preliminary results in this laboratory for 1,2-dichloroethane and 1,2-dibromoethane indicate a shortening of the C—C bond compared with that of ethane.[33] The observed shortening is, however, only 0·02 Å instead of the earlier reported shortening of 0·05 Å[34] for the chloro compound.

RINGS AND BENT BONDS

To study the influence of the so-called bent bonds it is important to measure the C—C bond lengths with the highest possible accuracy. The most important molecule in this connection is cyclopropane. Three independent electron-diffraction studies have been carried out on this molecule during the last few years. The structure parameters are: C—C distance 1·509 Å, C—H distance 1·091 Å, and HCH angle 113·8°. The estimated error limits are ±0·003 Å, ±0·01 Å and ±2° respectively.[35]

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[33] A. Almenningen, O. Bastiansen and J. Brunvoll, unpublished.

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

[35] A. Almenningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.* In press

For cyclobutane the best C—C and C—H distances obtained are 1·548 Å and 1·092 Å respectively.[36] The rather large C—C distance value is probably related to the repulsion between two carbon atoms in diagonal position. For cyclopentane a C—C distance of 1·539 Å is observed.[36] This is nearly the same as that observed for ethane.

Both the cyclobutane and cyclopentane molecule seem to deviate from the symmetric form with a four respectively fivefold axis of symmetry. This deviation seems to affect both the hydrogen atoms and the carbon atoms. Both molecules exhibit a non-planar carbon skeleton.

CONDENSED AROMATIC RING SYSTEMS

Electron diffraction studies on naphthalene, anthracene, and coronene[37,38] have been carried out, and the results are compared with those obtained by Cruickshank *et al.* using X-ray crystallographic methods.[39] Really reliable values have been obtained only for naphthalene, and they correspond very satisfactorily with those obtained by Cruickshank *et al.* Naphthalene should, therefore, be a good case for testing various theoretical approaches.

It is interesting to note the increase in the average C—C bond distance with the size of the molecules. The average C—C bond distances found by electron-diffraction studies for benzene, naphthalene, anthracene, and coronene are: 1·397, 1·401, 1·408 and 1·415 Å respectively. One could include graphite in this list with its C—C bond distance of 1·421 Å. By comparing graphite with the aromatic molecules mentioned one should, however, keep in mind the principal difference that exists. In graphite *p* electrons no doubt play some part in keeping the layers in the lattice together. For the free molecules as studied in the vapour phase all the *p* electrons are engaged within the molecule.

FREE AND RESTRICTED ROTATION

The problem of free and restricted rotation around a C—C bond is no doubt greatly dependent upon the bond environment. A large amount of experimental work has been done in this field and review articles[40,41] and books[42] have been devoted to the problem. The problem was also partly discussed earlier in this article. The only question we want to raise in this connexion is the following: Do carbon-carbon bonds around which there is entirely free rotation exist at all? One could think of molecules of the type as butyne-2. The sp^3-sp C—C bonds at the two ends of the molecule should not lead to restriction and the central triple bond should according to well established views have cylinder symmetry. Further the distance between the two methyl groups should be so large that no appreciable steric effect should be expected. Electron-diffraction studies on 1,4-dibromobutyne-2[43] and 1,4-dichlorobutyne-2[44] have been carried out. No detectable restriction is observed. Electron-diffraction studies, however, can not exclude a possible existence of a small potential barrier of say 100–200 cal/mole.

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SOME CONCLUDING REMARKS

The present contribution has come out more as a series of statements on experimental results than a real discussion of the theoretical aspects involved. The authors have considered this as their main task.

In concluding, we want to emphasize again the errors that occur in any experimental result. Being among those who are putting out distance values and other structure parameters on the market for the use by theoreticians we feel particularly responsible on this point. It should be remembered that precision measurements of structure parameters are difficult to carry out, but it is still more difficult to give a realistic evaluation of the error limits. Calculation of standard deviations gives no doubt a good indication of the relative error in various distances in the same molecule, and the study of reproducibility gives a good indication of the reliability of the method. However, each molecule presents the investigator with new problems and every new experiment may be obscured by unexpected irregularities.

These warnings are hoped to help avoiding elaborate theoretical calculations to be based upon experimental effects of dubious existence. Unfortunately many of the most interesting effects from a theoretical point of view correspond to structural changes on the limit of the experimental methods.