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INTERATOMIC DISTANCES IN NON-AROMATIC HYDROCARBONS IN THE LIGHT OF HYBRIDIZATION THEORY

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DEWAR and Schmeising,[1] Brown[2] and the author,[3] each independently have advanced the theory that the properties of molecules with multiple bonds are determined by hybridization of the carbon atoms rather than by the resonance effect. According to this concept the length and other physical parameters of the C—C σ-bond are a function of the valence states of the carbon atoms and vary widely depending upon whether this bond is adjacent to single or multiple bonds.

Subsequently, this highly important problem of the effect of hybridization and resonance on the properties of the chemical bond became the subject matter of discussion.

Mulliken[4] assumes that the length of the σ-bond is determined to the extent of 60% by hybridization of the carbon atom and 40% by delocalization of electrons. Samayajulu,[5] Lide[6] and Bastiansen and Trettenberg[7] expressed the opinion that hybridization is the principal factor determining the bond length resonance playing a minor role. Wilson[8] stated that hybridization theory explains the observed facts only qualitatively, but not quantitatively.

Evaluation of the relative roles played by hybridization and resonance is based mainly on a comparison of the experimental lengths of single bonds and the sum of the covalent radii, characteristic of a given valence state of the carbon atom. Naturally the covalent radii of carbon in the sp^3, sp^2 and sp states should be determined from data on the interatomic distances in molecules containing the carbon atom in the respective state. However; many authors utilize for this purpose molecules with bonds formed by carbon atoms in a non-integral hybridization state or, according to Moffit[9] in a state of second order hybridization.

For example, Lide[6] and Bastiansen and Trattenberg[7] take for the covalent radius

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[1] M. Dewar and H. Schmeising, *Tetrahedron* **5**, 166 (1959).

[2] M. Brown, *Trans. Farad. Soc.* **55**, 694 (1959).

[3] B. M. Mikhailov, *Izv. Acad. Nauk. USSR, Otdel. Khim. Nauk* 1379 (1960).

[4] B. Mulliken, *Tetrahedron* **6**, 68 (1959).

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

[6] D. Lide, *Tetrahedron* **17**, 125 (1962).

[7] O. Bastiansen and M. Trettenberg, *Tetrahedron* **17**, 147 (1962).

[8] E. Wilson, *Tetrahedron* **17**, 191 (1962).

[9] W. Moffit, *Proc. Roy. Soc.* A, **202**, 534 (1950).

of the sp^3 carbon half the interatomic distance in ethane (0·763 Å or 0·767 Å), although in this molecule the carbon atom is in a state intermediate between sp^3 and sp^2, the methyl HCH angle being less than 109° 28′.

Clearly one should take as covalent radius of sp^3 carbon half the interatomic distance in diamond, i.e. 0·772 Å. For the covalent radius of the sp^2 carbon could be taken the half length of the σ-bond in diphenyl[10] (1·489 ± 0·0075 Å), i.e. 0·745 Å, since the phenyl rings in this molecule are little distorted and are at an angle of 60° to each other, so that they are linked by an almost pure sp^2–sp^2 bond. Lide[6] determines the radius of the sp^2 carbon (0·738 Å) by subtracting the radius of the sp^3 carbon from the length of the σ-bond in propylene. Dewar and Schmeising[11] calculate the radius of the sp^2 carbon from the mean length of the σ-bond in butadiene, diphenyl and 4,4′-dipyridyl. It should be noted that the interatomic distances in propylene and butadiene cannot serve as the basis for determining the sp^2 radius since the carbon atoms in these molecules are not in a state of integral hybridization.

Experimental values for the length of the sp–sp bond in various compounds vary from 1·378 Å to 1·380 Å[11] (cyanoacetylene, 1·378 Å,[12] diacetylene 1·379 Å,[13] dicyan 1·380 Å[14]).

The system of covalent radii, selected on the basis of experimental data on the interatomic distances, is linearly related to the s-character of the carbon orbital, as expressed by the equation:

$$r_C^{\mathrm{cov}} = (0{\cdot}854 - 0{\cdot}328s)\ \text{Å} \tag{1}$$

It follows from Eq. 1, that the covalent radius of the p orbital of carbon is 0·854 Å and of the s orbital 0·526 Å.

An apparently strong argument against a system of covalent radii for carbon in the various valence states and against the theory of hybridization as a whole is the fact that the length of the C—H bond diminishes only by 0·031 Å on passing from methane to acetylene, whereas it is shorter by 0·07 Å in methylacetylene than in propane. The reduction in the length of the σ-bond in methylacetylene by more than 0·03 Å is regarded by some authors as the result of shift of the π electrons towards the single bond. Assuming a constant radius for hydrogen (0·323 Å) Coulson[15] finds the length of the sp carbon radius in acetylene from the length of the C—H bond to equal 0·735 Å.

The difference between the sum of the covalent radii of sp^3- and sp-carbon and the experimental values for the length of the single bond in methylacetylene (0·048 Å) is ascribed to resonance shortening of the bond.

Such evaluation of the covalent radii of carbon and of the effect of resonance (conjugation) and hybridization on the bond lengths is based on the assumption that the hydrogen radius is of a constant value whatever the type of C—H bond. However, this assumption is not justified. The orbitals of carbon of different hybridization differ in electronegativity; hence, depending on the valence state of carbon the

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[10] A. Almeningen and O. Bastiansen, *Kgl. Norcke Videnskab. Selskabs. Skrifter* N4, 1 (1958).

[11] M. Dewar and H. Schmeising, *Tetrahedron* **11**, 96 (1960).

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

[13] G. Graine and H. Thompson, *Trans. Farad. Soc.* **49**, 1273 (1953).

[14] C. Moller and B. Stoicheff, *Canad. J. Phys.* **82**, 635 (1954).

[15] C. Coulson, *Victor Henri Memorial Desoer* Liege, 15 (1948).

C—H bonds contain a greater or less amount of ionic character, which naturally affects the atomic radii.

Let us consider this question in somewhat more detail. From spectroscopic data on the lengths of the C—H bonds methane[16] (1·094 Å), ethylene[17] (1·086 Å) and acetylene[18] (1·061 Å) it follows that a linear relation given by Eq. 2 exists between the lengths of the C—H bonds and the s-character of the carbon orbital:

$$d(\text{C—H}) = (1{\cdot}127 - 0{\cdot}132s)\ \text{Å} \tag{2}$$

In a comparison of the lengths of the C—H bonds and valence states of carbon the fact that the HCH valence angle in ethylene is 117° 22′ has been taken into account, so that the s-character of the carbon orbital in the direction of the hydrogen atom is 0·315 rather than 0·333. To determine the s-character of the carbon orbitals in the case of non-integral hybridization use was made of the relations derived by Coulson.[15]

Hinze and Jaffe[19] have recently shown that there is also a linear relation between the s-character of the carbon orbitals and their electronegativity. The equation being:

$$\chi_{cj} = (5{\cdot}80 + 9{\cdot}15s)\ \text{eV} \tag{3}$$

(The electronegativity equals the half sum of the ionization potential and the affinity of a carbon orbital for an electron, $\chi = \frac{1}{2}(I_V + E_V)$. The points for $s = 0{\cdot}25$ and $s = 0{\cdot}33$ lie on a straight line at $\chi = 8{\cdot}09$ eV and $\chi = 8{\cdot}85$ eV respectively.)

In order to ascertain the effect of polarity of the C—H bond on its length it is necessary to first determine the covalent radius of hydrogen from Eqs. 1–3. For this purpose we assume the electronegativity of the carbon orbital to equal that of the hydrogen orbital (7·17 eV) and from Eq. 3 we find that the s-character of the carbon orbital in a non-polarized C—H bond equals 0·15. Then by means of Eq. 1 we find that for the given hybridization the radius of the carbon orbital is 0·805 Å, whereas the covalent hydrogen radius (from Eq. 2) is 0·302 Å.

For further treatment of this question we now turn to the orbital electronegativity concept as developed by Hinze *et al.*[20] which makes it possible to evaluate the influence of the polar factor on the length of the C—H bond. According to this concept when a bond is formed by atoms A and B differing in electronegativity, charge transfer occurs from the orbital of the less electronegative atom to that of the more electronegative atom. At equilibrium the orbitals of atoms A and B are of equal electronegativity (called by the authors bond electronegativity) localized on the orbitals with η_A and η_B electrons respectively ($\eta_A + \eta_B = 2$). The ionic character of the bond, i, is determined by the Eq. 4:

$$i = |n_{Aj} - 1| = \left|\frac{\Delta\chi}{2(C_A + C_B)}\right| \tag{4}$$

where η_A is the number of electrons on the j orbital of atom A, $\Delta\chi$ the difference in electronegativity between atoms A and B and C_A and C_B the half differences between

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[16] M. Thomas and H. Welsh, *Canad. J. Phys.* **38**, 1291 (1960).

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

[18] M. Christensen, D. Eaton, B. Green and H. Thompson, *Proc. Roy. Soc.* **238**, 15 (1956).

[19] J. Hinze and H. Jaffe, *J. Amer. Chem. Soc.* **84**, 540 (1962).

[20] J. Hinze, M. Whitehead and H. Jaffe, *J. Amer. Chem. Soc.* **85**, 148 (1963).

the ionization potentials and the electron affinities for the orbitals of A and B, respectively $[C = \frac{1}{2}(I_V - E_V)]$.

By means of Eq. 4 and data on the ionization potential and electron affinity of carbon in the sp^3, sp^2 and sp valence states[19] we obtain the values of η_C and η_H for the orbitals of carbon and hydrogen in methane and acetylene.

To find the number of localized electrons on the carbon and hydrogen orbitals in ethylene ($s = 0{\cdot}315$) we make use of the curves depicting I_V and E_V as function of the s-character of the carbon orbital.[19] The values of η_C are presented in the fourth column of Table 1.

TABLE 1

1	2	3	4	5	6	7	8	9	10
S	χ_{ev}	$\chi_C - \chi_H$	$\eta_C - 1$	r_C^{cov}	r_C^δ	$r_C^\delta - r_C^{cov}$	r_H^δ	$r_H^\delta - r_H^{cov}$	d(C—H)
0	5·80	−1·37	−0·051	0·854	0·810	−0·044	0·317	+0·015	1·127
0·15	7·17	0	0	0·805	0·805	0	0·302	0	1·107
0·25	8·09	0·92	0·034	0·772	0·802	0·030	0·292	−0·010	1·094
0·315	8·68	1·51	0·056	0·751	0·800	0·049	0·286	−0·016	1·086
0·333	8·85	1·68	0·063	0·745	0·800	0·055	0·283	−0·019	1·083
0·5	10·38	3·21	0·119	0·690	0·795	0·015	0·266	−0·036	1·061

As can be seen from Fig. 1, the number of electrons (n) localized on the carbon orbital in the C—H bond is linearly related to the s-character of the latter (Eq. 5):

$$n_C = (0{\cdot}949 + 0{\cdot}34s)\,e \tag{5}$$

In order to correlate n_i with the orbital radii in the C—H bond, the bond considered should have the covalent radius of hydrogen known, while the radius of the proton naturally can be taken as zero. If one now varies the radius of the hydride ion (H$^-$) within wide limits (from 0·5 Å to 0·8 Å), it follows from the smooth curves plotted by means of the three points ($r_{H^+} = 0$, $r_H^{cov} = 0{\cdot}302$ Å and $r_{H^-} = 0{\cdot}5$–$0{\cdot}8$ Å) that for n_H values approaching unity (0·90–1·05) the hydrogen orbital radii will differ by only ±0·003–0·004 Å from the values given by a linear dependence. Assuming a linear dependence to exist between n_H and the hydrogen orbital radii we obtain their values (to the above-mentioned accuracy) for different types of C—H bonds (column 8, Table 1.) Subtracting these values from the bond lengths in methane, ethylene and acetylene, the radii for the carbon orbitals in these molecules are found (column 6, Table 1). As can be seen from the Table (column 7) the covalent radius of carbon (0·772 Å) is increased by 0·03 Å in methane, whereas the radius for hydrogen diminishes by only 0·01 Å. If the atomic radii in the C—H bonds would not have contracted, the bond length in methane would have been 1·074 Å. In acetylene the orbital radius of carbon is greater by 0·105 Å, whereas the hydrogen radius is less by 0·036 Å, i.e. the bond length is augmented by 0·069 Å as compared with the sum of the covalent radii (0·992 Å).

The change in the orbital radii of carbon and hydrogen in the C—H bond is proportional to the difference in electronegativity of the carbon and hydrogen orbitals ($\Delta\chi$) (Eqs. 6 and 7).

$$\Delta r_C = 0{\cdot}0337\,(\Delta\chi)\ \text{Å} \tag{6}$$

$$\Delta r_H = 0{\cdot}0112\,(\Delta\chi)\ \text{Å} \tag{7}$$

For n_C values close to unity as in real hydrocarbon molecules the changes in the radius of the carbon atom are determined by Eq. 8:

$$\Delta r_C = 0{\cdot}882\,(n - 1) \tag{8}$$

It follows from Eqs 6 and 7 that the length of the C—H bond as a function of the electronegativity of the carbon orbital is expressed by Eq. 9:

$$d(\text{C—H}) = r_C^{\text{cov}} + r_H^{\text{cov}} + 0{\cdot}0215\,(\chi_C - \chi_H) \tag{9}$$

In the C_p—H bond the radius of the p orbital of carbon is reduced by 0·046 Å and the radius of hydrogen is increased by 0·015 Å, so that the over-all effect is a shortening of the bond by 0·029 Å as compared with the sums of the covalent radii. In real hydrocarbon molecules, when $\chi_C - \chi_H > 0$, the C—H bond is longer than the sum of the covalent radii.

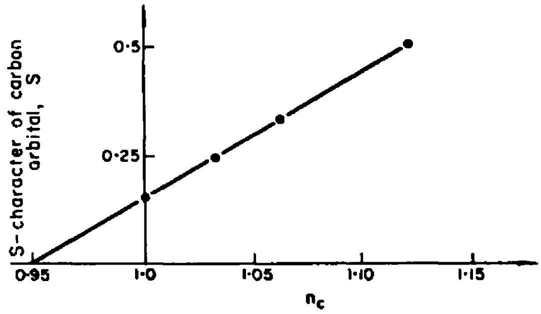

FIG. 1

According to Pauling,[21] an increase in the ionic character of a bond increases its energy and decreases its length owing to resonance of the covalent and ionic states. This is reflected in the empirical equation of Schomaker-Stevenson[22] (Eq. 10), corrected by Pauling[21] with respect to selection of the coefficients C for elements of different rows of the periodic system:

$$d(A - B) = r_A + r_B - C(\chi_A - \chi_B) \tag{10}$$

It follows from the foregoing that Pauling's conclusion regarding bond shortening with increase in the amount of ionic character is incorrect with respect to the C—H bond. This does not hold for bonds between hydrogen and other elements more electronegative than hydrogen. In hydrides of elements less electronegative than hydrogen the bond lengths are in fact less than the sums of the covalent radii. In such hydrides the radius of the element is shortened to a greater extent than the increase in length of the hydrogen radius.

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[21] L. Pauling, *The Nature of the Chemical Bond.* New York (1960).

[22] V. Schomaker and D. Stevenson, *J. Amer. Chem. Soc.* **63**, 37 (1941).

Utilizing the data on the electronegativity of the carbon orbitals in various valence states as well as Eq. 4, the degree of ionic character of the C—C bonds, $n_{C_i} - 1$, can be obtained. It follows from a consideration of the C—C bonds formed by sp-carbon and carbon atoms with other *s* characters of the orbital (0·15, 0·25, 0·315, 0·333) that n_{C_i} is linearly related to the electronegativity differences of the carbon atoms forming the bond.

The difference between the orbital radii of carbon in different valence states is comparatively small. One could therefore expect that in C—C bonds, when the values of n_{C_i} differ little from unity the lengthening of the radius of the more electronegative carbon orbital will differ very little from its shortening in the other carbon atom with the lower electronegativity, i.e. the length of the C—C bond should practically equal the sum of the covalent radii of the carbon atoms forming the bond. As will be seen in the following this holds for various types of hydrocarbons, including even methylacetylene in which the electronegativity of the carbon atoms is maximum.

In considering the structures of the various classes of aliphatic hydrocarbons in which the carbon atoms are in a state of non-integral hybridization, we use the relation between the covalent radii of the carbon orbitals and their *s*-character (Eq. 1).

Different values have been suggested for the length of the C—C bonds in ethane (1·534 Å,[23] 1·536 Å[24] and 1·5376 ± 0·003 Å[25]) and for the HCH angle (109° 11′, 109° 24′, 108° 48′ ± 0·5°, respectively). If the mean value (1·536 Å) is taken for the C—C bond length, then from Eq. 1 and the dependence of the *s*-character on the bond angles,[15] we find that for $r_C = 0·768$ Å the *s*-character of the carbon orbitals in their mutual direction is 0·262, and 0·246 in the direction of the hydrogen atoms; the HCH angle is then 109° 3′ (Table 2). In propane[26] the HCH angle of the CH_2 group is 106·1° ± 0·02°, the HCH angle of the methane group which is determined with an accuracy to only ±1° is 107° 42′ ± 1°. From these values we obtain the covalent radius in CH_3 as 0·755 Å and in CH_2 as 0·764 Å, which together give 1·519 Å, differing from the experimental value of the C—C bond length by 0·007 Å (Table 2). The difference is due to insufficiently accurate determination of the bond angles. From experimental data on the geometry of the isobutane molecule,[27] assuming the HCH angle in CH_3 to be 107° 52′ we find that the C—C bond length practically coincides with the experimental value of 1·525 + 0·001 Å. From data on the molecular structure of propylene[28] (for axial symmetry of the CH_3 group the HCH angle is 107° 42′) we find the length of the C—C bond to be 1·497 Å (Table 2), whereas the experimental value is 1·501 ± 0·004 Å. According to Bartell and Bonham,[29] the CCH_{methyl} angle in isobutylene is 110·4° ± 0·8°, the bond between the carbon atoms of the methyl group and the double bond is 1·505 ± 0·003 Å and the angle between the methyl groups is about 112° with the deviation from this value amounting to not more than 3–4°. From these data we find that $d(C^1—C^2) = 1·527$ Å, i.e. exceeds the experimental value by 0·022 Å.

Such large divergence between the experimental and calculated results is due to

[23] H. Allen and E. Plyer, *J. Chem. Phys.* **31**, 1062 (1959).

[24] A. Almeningen and O. Bastiansen, *Acta Chem. Scand.* **9**, 815 (1955).

[25] B. Stoicheff, *Canad. J. Phys.* **40**, 358 (1962).

[26] D. Lide, *J. Chem. Phys.* **33**, 1515 (1960).

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

[28] D. Lide and D. Christensen, *J. Chem. Phys.* **35**, 1374 (1961).

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

the fact that the angle between the methyl groups of isobutylene differs considerably from 112°. For $d(C^1—C^2) = 1{\cdot}505$ Å and the HCH angle in the methyl group equal 107° 42′ (as in propylene) the angle between the methyl groups should be 117° 40′. One may expect that on subsequent, more accurate determinations of the isobutylene structure the angle between the methyl groups will be found to be much closer to this value.

From the value of 108° 42′ for the HCH angle in methylacetylene[12] we find the length of the C—C bond to be 1·456 Å, which differs by 0·004 Å from the experimental value. In methylchloroacetylene,[30] acetonitrile[11] and methylcyanoacetylene[31] the C—C bond length is 1·458 Å, but the HCH angles between the methyl groups differ appreciably (108° 8′, 109° 30′ and 108° 30′, respectively). In such compounds the methyl group is bound to carbons of the same hybridization so that the HCH angles should not differ appreciably from each other. If the angle in methylacetylene is taken to be 108° 56′, the length of the C—C bond is 1·457 Å.

TABLE 2*

Compound	$s_{C'}$	$r_{C'}$	s_{C^2}	r_{C^2}	$d(C'—C^2)$ calcul.	$d(C'—C^2)$ exper.	Remarks
Ethane	0·262	0·768	0·262	0·768	1·536	1·536	HCH = 109° 3′
Propane	0·301	0·755	0·276	0·764	1·519	1·526 ± 0·002	
Isobutane	0·295	0·757	0·265	0·767	1·524	1·525 ± 0·001	
Propylene	0·301	0·755	0·343	0·742	1·497	1·501 ± 0·004	
Isobutylene	0·301	0·755	0·317	0·750	1·505	1·505 ± 0·003	$C'C^2C^2$ = 117° 40′
Methylacetylene	0·272	0·766	0·500	0·690	1·456	1·459	
Butadiene	0·336	0·744	0·336	0·744	1·488	1·484 ± 0·01	

* $s_{C'}$ is the *s*-character of the carbon orbital of the CH_3 group in the direction of the adjacent carbon atom, s_{C^2} is the *s*-character of the carbon orbital forming the bond with the methyl group; r_{C^1}, and r_{C^2} are the radii of the corresponding carbon orbitals; in butadiene s_{C^1}, and s_{C^2} are the *s*-characters of the carbon orbitals.

From the experimental data on the bond angles in butadiene[32] it follows that the length of the σ-bond in this compound should be 1·488 Å (Table 2), whereas the experimental value is 1·4830 ± 0·01 Å.

In cyclotetraene[33] the single bond is 0·021 Å shorter than in butadiene. To explain this difference it is assumed that the cyclic structure of this compound favours delocalization of the π-electrons.[7] Unfortunately the C═C—H angle in cyclooctatetraene was determined not very accurately (118·3 ± 5·9°) and one cannot say on the basis of the experimental data to what extent the length of the single bond (1·462 ± 0·001 Å) is in accord with the geometry of the molecule as a whole. If, however, the C═C—H angle be varied within the limits of error of the determination, then at a value of 116° 40′ the amount of *s*-character of the carbon single bond orbitals is 0·374 and the length of the C—C bond is 1·462 Å. Probably in subsequent, more accurate structural determinations of cyclotetraene the C═C—H angle will be found to be close to 117°.

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[30] C. Costain, *J. Chem. Phys.* 2037 (1955).

[31] J. Sheridan and L. Thomas, *Nature*, *Lond.* **174,** 798 (1954).

[32] A. Almeningen, O. Bastiansen and M. Trettenberg, *Acta Chem. Scand.* **12,** 1221 (1958).

[33] O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.* **27,** 1311 (1957).

It thus follows that the interatomic distances in saturated and unsaturated hydrocarbons are in good agreement with the hydridization theory. The observed dependence between the s-character of the carbon orbitals and their radii holds also for unsaturated hydrocarbons. If the resonance effect (conjugation) had a bearing on the interatomic distances in such molecules, then they would not have obeyed Eq. 1. Delocalization of the π-electrons would have led to a noticeable shortening of the σ-bonds, adjoining the multiple bonds, as compared with σ-bonds in saturated hydrocarbons.

From the experimental data on the bond lengths in ethylene, allene[34] (1·309 Å) and butatriene[35] (1·284 ± 0·005 Å) it follows that the shortening of the σ-bond

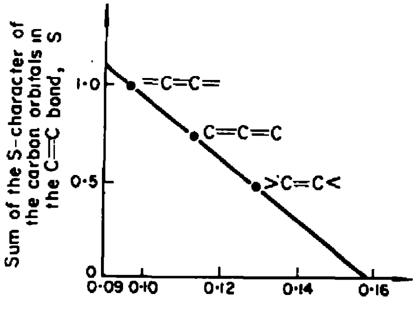

FIG. 2

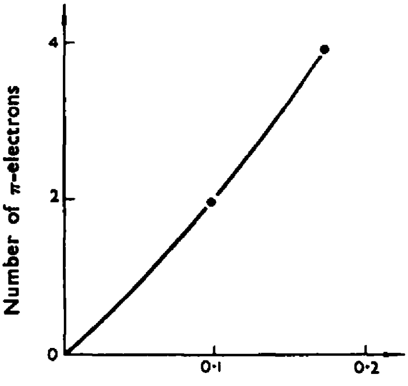

FIG. 3

(Δd) under the influence of the π-bond is linearly related to the s-character of the carbon orbital (Fig. 2). In plotting the curve in Fig. 2, the s-character of the carbon orbital in ethylene and the end carbon atoms in allene being 0·37, was taken into account so that the sum of the s-character of the carbon orbital in ethylene is 0·74 and in allene is 0·87. The shortening of the σ-bond (Δd) by one π-bond is given by Eq. 13.

$$\Delta d = (0{\cdot}223 - 0{\cdot}127(s_1 + s_2)/\text{A} \qquad (13)$$

The shortening of the σ-bond relevant to the number of π-electrons localized on the bond is also a function of the s-character of the carbon orbitals. For sp–sp bonds this dependence can be derived from data on the interatomic distances in acetylene[36] (r_0 = 1·207Å, r_c = 1·205 Å) and butatriene. It can be seen from Fig. 3 (in acetylene Δd = 0·174 Å) in butatriene (Δd = 0·096 Å for the central bond) that on delocalization of only 0·1 of a π-electron (2·5% of the total number of π-electrons) the triple bond should become longer by 0·004 Å. However, it is known from experiment that the length of the triple bond in acetylene derivatives practically does not differ from that in acetylene itself. In methylacetylene[12] it is 1·208 Å (1·205 Å), in cyanoacetylene[12] 1·205 Å, in methylcyanoacetylene 1·205 Å[37] and in dimethyldiaceylene 1·207 Å.[7]

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[34] B. Stoicheff, *Canad. J. Phys.* **33**, 811 (1955).
[35] B. Stoicheff, *Canad. J. Phys.* **35**, 837 (1957).
[36] J. Collomon and B. Stoicheff, *Canad. J. Phys.* **35**, 373 (1957).
[37] L. Thomas, J. Heeks and J. Sheridan, *Arch. Sci. Geneva* **10**, 18 (1957).

Hence one may conclude that within the limits of error of interatomic distance determinations (0·002 Å) hyperconjugation (static effect of the σ, π conjugation) and conjugation (static effect of π, π conjugation) have no experimental backing. Even a very small shift of the π-electrons of the multiple bond onto the adjacent single bond would have been revealed by modern methods of measuring interatomic distances.

CONCLUSIONS

Data on interatomic distances confirm the theory of hybridization according to which the bond lengths of non-aromatic hydrocarbons are determined by the valence states of the carbon atoms.

No resonance effect [hyperconjugation (σ, π conjugation) in the case of olefinic hydrocarbons and conjugation (π, π conjugation) in hydrocarbons with alternating single and multiple bonds] has been detected experimentally (from data on molecular geometry).