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THE DISTRIBUTION OF THE PI ELECTRONIC CHARGE OF THE CARBON—CARBON TRIPLE BOND

P. POLITZER*

Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122

and

R. R. HARRIS†

Department of Chemistry, Indiana University, Bloomington, Indiana 47401

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Abstract—It is shown that about 40% of the pi electronic charge of the C—C "triple" bond in acetylene, fluoroacetylene, and lithium acetylene is outside of the C—C internuclear region. Accordingly, it seems appropriate to describe these bonds as being made up of one sigma bond and two half pi bonds. The pi charge outside of the C—C region is concentrated primarily in the neighboring bond region, which suggests a very direct explanation for the observed shortening of a single bond by the presence of an adjacent multiple bond.

INTRODUCTION

THE acetylene molecule provides the classic example of the C—C triple bond, generally described as being composed of one sigma and two pi bonds. The pi bonds are known to be weaker than the sigma, a fact which is commonly attributed to the lesser extent of overlap between $2p\pi$ atomic orbitals, as compared to *sp* hybrid orbitals.‡

The C—H bond in acetylene is also of interest, particularly when compared to the same bond in ethane. Table 1 presents the bond lengths, force constants, and dissociation energies of these bonds. These data indicate very clearly that the C—H bond is considerably stronger in acetylene than in ethane, a conclusion which is consistent with the observed phenomenon that a single bond is shortened by the presence of an adjacent multiple bond.§ The cause of this shortening is a matter of some controversy. It is often explained as a hybridization effect;[2, 3] in the present case, for instance, it would be argued that the greater *s* character of the C atom's hybrid orbitals in acetylene, compared to ethane, means that its effective atomic radius is less in the former case, and the C—H bond is consequently shorter. Other explanations have also been proposed, however, invoking the concepts of conjugation and hyperconjugation, and steric hindrance.[2]

Another interesting comparison can be made between acetylene and fluoroacetylene. It might reasonably be anticipated that the presence of an adjacent F atom would have some significant effect upon the properties of the C—C triple bond,

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* To whom correspondence concerning this article should be addressed.

† Present address: Control Data Corporation, 15 Spinning Wheel Road, Hinsdale, Illinois, 60521.

‡ For example, the value of the overlap integral between two carbon *sp* hybrid orbitals, at an internuclear distance of 1·24 A, is 0·86, while for two $2p\pi$ orbitals it is 0·32 (Ref 1).

§ A critical review of various theories concerning this effect has been given by E. B. Wilson, Jr. (Ref 2).

particularly in view of the possibility of a contributing resonance structure of the form $H-C^-=C=F^+$. The contribution of this structure has indeed been invoked as the reason for the fact that the C—F bond is so much stronger in fluoroacetylene than in, for example, fluoroethane (see Table 1).[4, 5,*] However, the experimentally-determined properties of the C—C bonds in the two molecules do not reveal any marked effect of the F atom. Table 1 shows that the bond lengths and the force constants are very similar in the two cases.

Evidence will be presented in this paper which indicates that the traditional picture of the C—C triple bond should be modified somewhat, to take account of the fact that a very significant portion of its pi electronic density is not in the bonding region. Recognition of this situation permits a fuller and more fundamental understanding of the experimental data which are presented in Table 1.

TABLE 1. EXPERIMENTALLY-DETERMINED BOND PROPERTIES

Bond	Molecule	Bond length[a]	Force constant	Bond dissociation energy[b]
C—H	C_2H_6	1·093A	4·79 mdyne/A[c]	98 kcal/mole
C—H	C_2H_2	1·058	5·85[c]	~125
C—H	C_2HF	1·053	6·06[d]	
C—F	C_2H_5F	1·375	5·96[e]	106
C—F	C_2HF	1·279	8·64[d], 8·8[f]	
C—C	C_2H_6	1·534	4·50[c]	88
C—C	C_2H_2	1·204	15·85[f]	230
C—C	C_2HF	1·198	15·80[d], 15·4[f]	

[a] *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Main Volume and Supplement, Special Publications Nos. 11, 18, The Chemical Society, London, 1958 and 1965; J. K. Tyler and J. Sheridan, *Proc. Chem. Soc.* 119 (1960)

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CALCULATIONS AND RESULTS

Detailed descriptions of the electronic structures of acetylene, fluoroacetylene, and lithium acetylene can be obtained from the extended-basis-set self-consistent-field wave functions which are now available for these molecules.† These functions are believed to be close to the Hartree–Fock limit, and should therefore give good results,

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[*] It is relevant at this point to mention that a recent calculation of the atomic charges in fluoroacetylene yielded only a very small negative value (−0·05) for the fluorine (Ref 6). Considerable evidence supporting this result was cited.

[†] The wave functions used were taken from Ref 7, and had the following size basis sets: (12, 12, 6) for HCCH, (24, 10) for HCCLi, and (28, 14) for HCCF.

of first-order accuracy, for one-electron properties, such as electronic density distributions.[8, 9]

By integrating the electronic density function of a molecule over any given region of space within the molecule, one can determine the quantity of electronic charge in that region. Table 2 presents the results of integrating the valence electronic densities of acetylene, fluoroacetylene, and lithium acetylene over the regions bounded by planes perpendicular to the molecular axes at the positions of the nuclei. These numbers represent, therefore, the quantities of valence electronic charge in the various internuclear regions.

TABLE 2. AMOUNTS OF VALENCE ELECTRONIC CHARGE IN VARIOUS REGIONS[a]

Molecule	*Type of charge*	*Region*								
			H		C		C		X[b]	
	Sigma	0·41		1·59		1·99		1·59		0·41
HCCH	Pi	0·03		0·80		2·35		0·80		0·03
	Total	0·44		2·39		4·34		2·39		0·44
	Sigma	0·41		1·58		1·92		2·28		1·81
HCCF	Pi	0·03		0·84		2·46		2·83		1·84
	Total	0·44		2·42		4·38		5·11		3·65
	Sigma	0·43		1·59		2·08		1·85		0·04
HCCLi	Pi	0·04		0·86		2·30		0·80		0·01
	Total	0·47		2·45		4·38		2·65		0·05

[a] The data are given in units of electronic charge.
[b] X = H, F, or Li.

DISCUSSION

Considering first the region between the carbon nuclei, there is seen to be a striking similarity between acetylene and fluoroacetylene. The quantities of electronic charge contained in this region, both sigma and pi, are very nearly the same. This is in agreement with the experimental data discussed earlier, which indicate that the properties of the C—C bond are essentially the same in the two molecules.

Of particular interest and importance is the fact that whereas the amount of sigma charge in the C—C region is, for each of the three molecules, approximately 2·0 electrons, the quantity of pi charge per pi bond is only about 1·2 electrons. Thus, about 40 % of the pi electronic charge of the C—C bond in acetylene, fluoroacetylene, and lithium acetylene is *not* in the region between the carbon nuclei. This presumably comes about because these pi molecular orbitals are formed from atomic orbitals which are perpendicular to the molecular axis, with exactly half of the pi electronic charge initially being outside of the C—C region. Only about 20% of this outer charge shifts into the C—C region in the process of bond formation. These facts are brought out more clearly by Fig 1, which compares the charge density distributions of the pi electrons in acetylene and a $2p\pi$ atomic orbital on a free carbon atom.[10] The considerable amount of pi electronic charge which remains outside of the C—C region is clearly seen.

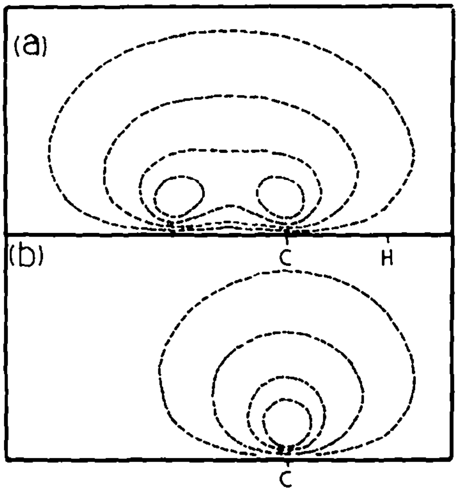

FIG 1. (a) The charge density distribution of the pi electrons in acetylene. The contours correspond to charge densities of 0·1, 0·01, 0·005 and 0·001 electrons/au^3, starting with the innermost contour.

(b) The charge density distribution of a $2p\pi$ atomic orbital of a free carbon atom. The contours correspond to the same charge densities as in (a).

A similar situation exists in the C—H bonds in these molecules. A very significant portion of the hydrogen $1s$ electronic charge remains outside of the C—H region, and the sigma charge binding the carbon and hydrogen nuclei is provided mainly by the carbon.

It should be mentioned that not all of the pi charge that is outside of the C—C regions is ineffective in binding the carbon nuclei; it has been shown that a small portion of the electronic charge *outside* of an internuclear region has, electrostatically, a slight net binding effect upon the nuclei.[11] This should be of relatively little consequence, however, and is probably more than balanced by the electrostatic bond-weakening effect of the remainder of the outer pi charge.[11]

Thus, it is somewhat misleading to say that there is a triple bond between the carbons in acetylene. Relative to the sigma bond, each of the pi bonds is more like a half bond. There has recently been proposed an operational definition of bond order, which requires only force constants and bond lengths (quantities which can be determined experimentally) and does not involve any wave functions.[12] It is encouraging to find that this definition, when applied to the C—C bonds in acetylene and fluoroacetylene, indicates bond orders of 2·02 for both molecules; for ethane, the value calculated is 0·95.

It is also interesting that the amount of pi charge which has been found in the C—C region of acetylene in the present work, using an *ab initio* near-Hartree-Fock molecular wave function, does not differ greatly from that found earlier by semi-empirical techniques. Ham and Ruedenberg, using free-electron theory, calculated the pi-bond population of acetylene to be 2·436 electrons; using pi-electron theory, they obtained a value of 2·400.[13] Bykov estimated the same quantity by several methods involving correlations with various molecular properties, and obtained values ranging from 2·27 to 2·59.[14] In his words, these results lead "to the breakdown of the traditional point of view, according to which there is a . . . four-π-electron C—C bond in [acetylene]." The present work puts this conclusion on a much firmer theoretical basis.

Although the pi electronic charge which is outside of the C—C region in acetylene is not effective in binding the carbon nuclei, it should play a definite role in binding the carbon and hydrogen nuclei, since this outer pi charge is primarily concentrated in the C—H region. Table 2 shows that the C—H regions of acetylene, fluoroacetylene, and lithium acetylene contain pi electronic charges of 0·80 to 0·86 electrons. This is thus a very direct explanation of the fact that the C—H bonds are stronger, and shorter, in acetylene than in ethane, in which there is no pi charge; the greater strength of the C—F bond in fluoroacetylene, as compared to fluoroethane, can to a large extent be interpreted in the same manner. This explanation does not depend upon considerations of the degree of *s* character, nor does it require that such concepts as hyperconjugation be invoked. One may indeed speculate that perhaps the presence of such "outer" pi charge is in general a key factor in the observed shortening of single bonds adjacent to multiple bonds. Bykov has developed semi-empirical equations for calculating the effects of such pi charges upon bond properties, and has obtained some impressive results.[14]

In each of the molecules studied in this work, a significant amount of pi electronic charge has been found to be in the bonding region adjacent to the multiple bond; thus, these "single" bonds can be said to have some pi character. Their properties reflect the presence of this extra bonding charge. The existence of this pi character does not require any concomitant weakening of the multiple bond, however, contrary to the implications of the resonance contributing structures which are commonly drawn to represent such situations; the pi charge involved is inherently outside of the C—C region.

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