

Structural Studies of Some Acetylene Derivatives by the CNDO/2 Method

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A problem of current interest in structural chemistry is the effect of the environment on carbon-carbon bonds. Among the different types of C-C bonds the triple bond is regarded as almost uninfluenced by the substituents.¹ The single bond adjacent to a triple bond may be more sensitive to environments. Microwave investigations show only minor variations in the C(sp)-C(sp³) distance where a CH₃ group was replaced by a CF₃ group in a number of acetylene derivatives.²⁻⁵ However, when both CH₃ groups in 2-butyne are replaced by CF₃, electron diffraction investigations show that the single bond increases by 0.012 Å.^{6,7} The results also indicate a minor shortening of the triple bond. Recently, Pople and Gordon⁸ used the CNDO/2 method to investigate the substituent effect of fluorine in some simple aliphatic compounds. The aim of the present paper was to study the effect of a CF₃ group in some acetylene derivatives by means of the CNDO method.

Method of calculation. The basic approximations involved in the CNDO calculations have been described previously.⁹⁻¹² The version of CNDO used in this study is the standard CNDO/2 with the necessary parameters taken from Pople and Segal.¹⁰

The molecular geometry used in the calculations of charge distribution and dipole moments was chosen to agree with values determined experimentally, when such were available. Reasonable values for the remaining compound (perfluoropropyne) were estimated. The total energy was calculated by varying the C(sp)-C(sp³) distance in steps of 0.001 Å, keeping the other molecular parameters constant. The bond distance giving the lowest total energy was taken as the equilibrium bond distance.

Results. The CNDO/2 method has been used to calculate the C(sp)-C(sp³) bond distances, charge distributions and electric dipole moments in propyne, 1,1,1-trifluoropropyne, 1-chloro-1-propyne, 3,3,3-trifluoro-1-chloropropyne, perfluoropropyne,

2-butyne, and perfluoro-2-butyne. Below, some of the details will be described.

(a) *The C(sp)-C(sp³) distance.* The

calculated $\equiv\text{C}-\text{C}-$ distances are given in

Table 1, together with available experimental results. The calculations indicate

Table 1. Calculated and observed C(sp)-C(sp³) distances (in Å).

Molecule	Calculated	Experimental	Ref.
CH ₃ -C≡C-H	1.431	1.459 ± 0.003	2
CF ₃ -C≡C-H	1.452	1.460 ± 0.02	3
CH ₃ -C≡C-Cl	1.426	1.458 ± 0.005	4
CF ₃ -C≡C-Cl	1.448	1.454 ± 0.006	5
CH ₃ -C≡C-CH ₃	1.431	1.466 ± 0.004	6
CF ₃ -C≡C-CF ₃	1.451	1.478 ± 0.003	7
CF ₃ -C≡C-F	1.447		

that a substitution of CH₃ by CF₃ increases the adjacent C(sp³)-C(sp) bond length by about 0.02 Å. Experimentally, this trend is only found for perfluoro-2-butyne.⁷

(b) *Charge distribution.* In order to investigate a possible correlation between charge distribution and bond lengths the total charge was divided among orbitals of the appropriate symmetry. Assuming a staggered conformation, 2-butyne and perfluorobutyne have D_{3d} symmetry while the other molecules have C_{3v} symmetry. Accordingly the molecular orbitals for 2-butyne and perfluoro-2-butyne belong to one of the irreducible representations A_{1g}, A_{1u}, A_{2g}, A_{2u}, E_g or E_u and to the representations A₁, A₂ or E for the other molecules. In the linear part of the molecules with C_{3v} symmetry the σ orbitals correspond completely to A₁ symmetry and the π orbitals to E symmetry. For the molecules of D_{3d} symmetry A_{1g}+A_{2u}, A_{2g}+A_{1u} and E_g+E_u effectively correspond to the representations A₁, A₂ and E for the C_{3v} molecules, respectively. In Table 2 the electron density *q* in the irreducible representations A₁ and E is given for the CX₃ (X=F,H) and C≡C groups of the molecules. Orbitals of A₂ symmetry occurred only for the CF₃ groups (one orbital on each CF₃ group), and these are not included in Table 2. Table 2 also contains the net charge displacement Δ*q* from

Table 2. Calculated charge divided into the different symmetries.

Molecule	Part of the molecule	A_1		E	
		q	Δq	q	Δq
$\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$	CH_3	2.988	0.012	3.966	0.034
	$\text{C}\equiv\text{C}-\text{H}$	5.012	-0.012	4.034	-0.034
$\text{CF}_3-\text{C}\equiv\text{C}-\text{H}$	CF_3	6.982	0.018	16.014	-0.014
	$\text{C}\equiv\text{C}-\text{H}$	5.018	-0.018	3.986	0.014
$\text{CH}_3-\text{C}\equiv\text{C}-\text{Cl}$	CH_3	2.973	0.027	3.954	0.046
	$\text{C}\equiv\text{C}-\text{Cl}$	7.027	-0.027	8.046	-0.046
$\text{CF}_3-\text{C}\equiv\text{C}-\text{Cl}$	CF_3	6.972	0.028	16.012	-0.012
	$\text{C}\equiv\text{C}-\text{Cl}$	7.028	-0.028	7.988	0.012
$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3^a$	CH_3	5.972	0.028	7.940	0.060
	$\text{C}\equiv\text{C}$	4.028	-0.028	4.060	-0.060
$\text{CF}_3-\text{C}\equiv\text{C}-\text{CF}_3^a$	CF_3	13.928	0.072	16.008	-0.008
	$\text{C}\equiv\text{C}$	4.072	-0.072	19.992	0.008
$\text{CF}_3-\text{C}\equiv\text{C}-\text{F}$	CF_3	6.959	0.041	16.022	-0.022
	$\text{C}\equiv\text{C}-\text{F}$	7.041	-0.041	7.978	0.022

^a For this molecule A_1 means $A_{1g} + A_{2u}$ and E means $E_g + E_u$ (see text).

the CX_3 groups. It is noteworthy that the Δq 's in A_1 are similar when the length of the single bond is not affected by the substitution, but different when an increase is observed (for perfluoro-2-butyne).⁷

(c) *Dipole moments.* The calculated dipole moments are compared with available experimental values in Table 3, using micro-

Table 3. Calculated and experimental dipole moments (in Debye).

Molecule	Calculated	Experimental	Ref.
$\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$	0.40	0.75 ± 0.01	2
$\text{CF}_3-\text{C}\equiv\text{C}-\text{H}$	2.43	2.36 ± 0.04	3
$\text{CH}_3-\text{C}\equiv\text{C}-\text{Cl}$	2.11	—	
$\text{CF}_3-\text{C}\equiv\text{C}-\text{Cl}$	1.49	1.73 ± 0.20	5
$\text{CF}_3-\text{C}\equiv\text{C}-\text{F}$	1.77	—	
$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$	0.0	0 ^a	
$\text{CF}_3-\text{C}\equiv\text{C}-\text{CF}_3$	0.0	0 ^a	

^a Due to symmetry.

wave data where possible. The results are generally in satisfactory agreement, indicating that the charge distributions in the molecules as reported above are reasonably reproduced by the CNDO/2 method.

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