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A Theoretical Study of the Structure and Charge Distribution of Some Alkynylcarbenium Ions

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Abstract: We have carried out STO-3G minimal basis set "ab initio" calculations to determine the structure and charge distribution, using the YSP population analysis, of the propargyl cation and some of its mono-, di-, and trisubstituted derivatives. Our results indicate that progressive α substitution favors a greater participation of mesomeric form $XYC_\alpha^+ - C_\beta{=}C_\gamma - Z$, while γ substitution increases the contribution of form $XYC_\alpha{=}C_\beta{=}C_\gamma^+ - Z$. The relative stability of the different derivatives is also discussed.

I. Introduction

Alkynylcarbenium ions were directly observed first by Richey, Philips, and Rennick[1] in 1965. Ever since, the number of experimental and theoretical studies on these (and related) cations has been considerable.[2] This interest is justified because alkynyl cations are directly related to and can be a convenient model[3] for vinyl cations, which are, in turn, intermediates in solvolyses of vinyl halides,[4-7] vinyl triflates,[7,8] and the electrophilic addition to alkynes.[9]

Alkynyl cations can exist in the two mesomeric forms presented in Figure 1.

Since the paper of Richey et al.[1] was published, a considerable experimental effort was devoted to studying the inherent stabilities, structure,[10,11] and charge distribution[3] of these cations. This last aspect constitutes one of the most recent and interesting applications of ^{13}C magnetic resonance spectroscopy, since it has been proved[12] that chemical shifts reflect the charge densities on carbons of similar hybridization and substitution.

All these experimental studies[3,10,11] indicate that mesomeric form II is an important contributor to the stability of these cations. However, little can be said on how substituents might change the relative importance of these mesomeric forms, because only tertiary ions are stable, and this makes observation of electronic changes at C_α, C_β, or C_γ impossible.[3] However, theoretical work can yield valuable information on this problem.

The first members of this family, propargyl cation and its possible isomers, have been already studied at the "ab initio" level, using different basis sets.[13] However, no effort was devoted to evaluate the structure and charge distribution of alkynyl cations, with the only exception being the semiempirical calculations of Pittman et al.[14]

In this paper we present an "ab initio" study of some alkynylcarbenium ions. We will center our discussion on the relative stability of mesomeric forms I and II and on the influence of the substituents on the stability of either form, in each particular case. We will calculate the charge distribution using the YSP population analysis,[15] which has been proved very reliable[16] to evaluate charge densities in neutral and charged systems.

YSP population analysis is a density-partitioning technique based on the representation of the electron density $\rho(r)$ by an expansion in terms of spherical atomic density basis functions which do not present the limitations of the Mulliken population analysis, in the sense that the charge distributions obtained do not depend on the details of the basis set used in spanning the molecular wave function.

II. Calculations

We have carried out a geometry optimization of these mono-, di-, and trisubstituted propargyl cation derivatives (**III**a–l), presented in Figure 2, using a STO-3G minimal basis set.[17]

In the optimization process for **III**b–f, the following restrictions were adopted: the methyl group was kept unchanged, assuming local C_{3v} symmetry with CH bond lengths equal to 1.10 Å and HCH bond angles equal to 109.47°. For **III**l cation, the NH_2 group was also kept unchanged and in the same plane of the molecule, assuming local C_{2v} symmetry with NH bond length equal to 1.0 Å and the NHN bond angle equal to 120°. In all cases (**III**a–l) we have taken the C_α–C_β–C_γ skeleton as linear.

With these restrictions, all the remaining parameters were optimized, until changes in the total energy were less than 10^{-5} au for variations of ±0.005 Å in the bond lengths and 0.1° in the bond angles.

III. Monosubstituted Derivatives

We present in Table I the optimized geometry of propargyl

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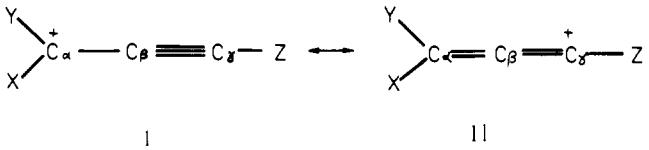
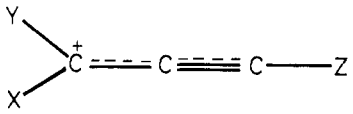
Table I. Geometrical Parameters for Propargyl Cation and Its Monosubstituted Derivatives in the Conformation of Minimal Energy

	IIIa	IIIb	IIIc	IIIg	IIIh	IIII
			Bond Lengths (Å)			
C_α-C_β	1.360	1.348	1.380	1.351	1.397	1.319
C_β-C_γ	1.214	1.222	1.204	1.237	1.198	1.242
C_α-X	1.109	1.106	1.110	1.107	1.120	1.099
C_α-Y	1.109	1.106	1.515	1.107	1.292	1.099
C_γ-Z	1.091	1.484	1.070	1.280	1.089	1.294
			Bond Angles (deg)			
$C_\beta C_\alpha X$	121.1	121.4	117.6	121.2	121.8	121.3
$C_\beta C_\alpha Y$	121.1	121.4	124.0	121.2	121.6	121.3
$XC_\alpha Y$	117.8	117.2	118.4	117.6	116.6	117.4
			Energies (au)			
	−113.563 92	−152.179 40	−152.175 10	−211.022 75	−211.037 48	−167.955 02



I II

Figure 1. Mesomeric forms of alkynylcarbenium ions.



		X	Y	Z
III	a	H	H	H
	b	H	H	CH_3
	c	H	CH_3	H
	d	H	CH_3	CH_3
	e	CH_3	CH_3	H
	f	CH_3	CH_3	CH_3
	g	H	H	F
	h	H	F	H
	i	H	F	F
	j	F	F	H
	k	F	F	F
	l	H	H	NH_2

Figure 2. Alkynyl cations included in this study.

cation[13] and its F- and CH_3-monosubstituted derivatives. The inclusion of IIII cation in this table will be justified later.

It is clear, from values in Table I, that α substitution (IIIc,h) considerably increases the C_α–C_β bond length and shortens the C_β–C_γ bond relative to the parent cation (IIIa), indicating that this substitution favors a considerable contribution of form I. On the contrary, γ substitution (IIIb,g) yields shorter C_α–C_β and larger C_β–C_γ bonds than those in the parent cation, which is evidence that γ substitution increases the participation (see Figure 1) of form II.

It is also evident that a different mechanism must be involved in these effects, since the substituents are of a very different nature. To study this aspect of the problem, we have evaluated the charge distribution of these cations, using the YSP population analysis.[15] The results obtained are presented in Figure 3.

Fluorine substitution at C_α increases considerably the charge on this carbon, stabilizing a structure with more participation of form I (see Figure 1). Obviously, γ substitution has the same effect on the γ-carbon atom, increasing the contribution of form II.

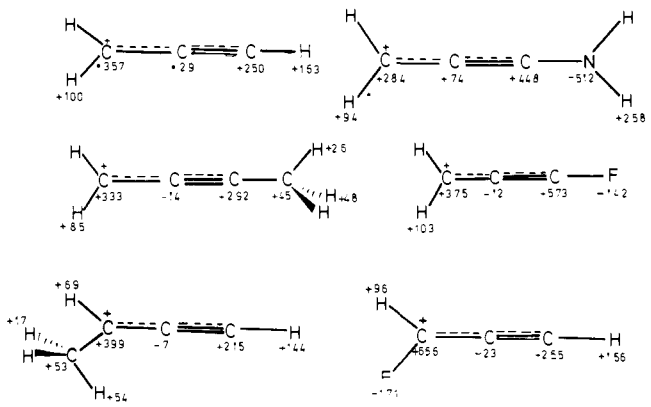


Figure 3. Charge distribution (10^{-3} electron) of propargyl cation and its monosubstituted derivatives, obtained using YSP population analysis and a STO-3G basis set.

When the substituent is a methyl group there is no substantial increase of the charge on the substituted carbon atom (see Figure 3). As it has been shown[18] that hyperconjugation is particularly intense in ionic species, we will analyze the π-electron density on these cations. Mulliken electron charge densities in the p_y orbitals (perpendicular to the molecular plane) are given in Table II for IIIa–c species. We can observe that methyl α substitution produces a decrease of the π charge density at C_α and an increase at C_β and C_γ, favoring a greater participation of form I, while the opposite effect is observed when substitution takes place at the γ carbon, favoring the participation of mesomeric form II.

In general, our results show that, if Y (see Figure 1) is a substituent that either withdraws σ electrons from C_α or donates π charge into the $2pC_\beta$ orbital, participation of form I is favored. When substituent Z (see Figure 1) presents the same behavior, a greater participation of form II occurs.

These effects are more intense in the case of fluorine substitution, because fluorine not only withdraws σ electrons from C_α, but also donates π charge into the $2pC_\beta$ orbital to a considerable extent.

It is also interesting to note that the α-substituted fluorine derivative (IIIh) is more stable than the γ-substituted one (IIIg). When the substituent is a methyl group the situation

Table II. Electron Density in the p_y Orbital of IIIa, IIIb, and IIIc Alkynyl Cations

	IIIa	IIIb	IIIc
C_α	0.409	0.472	0.391
C_β	1.129	1.126	1.135
C_γ	0.462	0.456	0.544

Table III. Geometrical Parameters for Di- and Trisubstituted Propargyl Cation Derivatives in the Conformation of Minimal Energy

	IIId	IIIe	IIIf	IIIi	IIIj	IIIk
			Bond Lengths (Å)			
C_α-C_β	1.365	1.395	1.381	1.384	1.413	1.399
C_β-C_γ	1.212	1.197	1.204	1.203	1.193	1.196
C_α-X	1.107	1.524	1.525	1.118	1.299	1.302
C_α-Y	1.516	1.524	1.525	1.296	1.299	1.302
C_γ-Z	1.485	1.084	1.486	1.283	1.090	1.285
			Bond Angles (deg)			
$C_\beta C_\alpha X$	118.0	120.0	120.4	121.7	122.7	122.9
$C_\beta C_\alpha Y$	124.1	120.0	120.4	121.9	122.7	122.9
$XC_\alpha Y$	117.9	120.0	119.2	116.4	114.6	114.2
			Energies (au)			
	−190.787 08	−190.781 99	−229.390 855	−308.494 57	−308.513 96	−405.970 10

Table IV. Geometrical Parameters for Propargyl Cation and Its Monosubstituted Derivatives in the Conformation of Minimal Energy (4-31G Basis)

	IIIa	IIIb	IIIc	IIIg	IIIh
			Bond Lengths (Å)		
C_α-C_β	1.336	1.328	1.353	1.329	1.348
C_β-C_γ	1.216	1.225	1.209	1.219	1.206
C_α-X	1.076	1.086	1.077	1.087	1.089
C_α-Y	1.076	1.086	1.475	1.087	1.293
C_γ-Z	1.061	1.444	1.070	1.257	1.089
			Bond Angles (deg)		
$C_\beta C_\alpha X$	120.9	121.1	117.1	121.0	123.9
$C_\beta C_\alpha Y$	120.9	121.1	124.4	121.0	122.2
$XC_\alpha Y$	118.2	117.8	118.5	118.0	113.9
			Energies (au)		
	−114.791 99	−153.803 50	−153.797 38	−213.479 69	−213.502 45

is the opposite and the γ-substituted cation is more stable. This can be explained in the following manner.

A fluorine atom withdraws σ electrons from C_α (or C_γ) and donates π charge into the $2pC_\beta$ orbital; this effect is particularly favored when the fluorine atom is bonded to the α carbon,[19] and therefore the α isomer must be the most stable one. On the contrary, the hyperconjugation effect is favored by linearity of the carbon framework; therefore, a methyl group is most stabilizing at the γ position.

To confirm that π donation is the mechanism involved in methyl substitution, we have carried out similar calculations for the γ-amino substituted derivative (IIII), where this effect must be particularly strong. The results obtained (see Table I) do confirm our previous conclusions, since the shortening of the C_α-C_β bond and the lengthening of the C_β-C_γ bond are much more important in this compound than in the γ-methyl substituted derivative (IIIb).

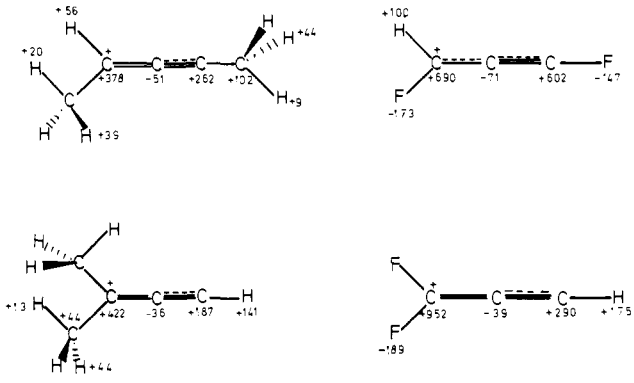


Figure 4. Charge distribution (10^{-3} electron) of disubstituted propargyl cation derivatives.

IV. Di- and Trisubstituted Derivatives

We present in Table III the optimized geometries of di- and trisubstituted propargyl cation derivatives.

Our results show that α,α substitution emphasizes the lengthening of the C_α-C_β bond relative to the α-monosubstituted derivatives (1.395 vs. 1.380 Å for methyl groups and 1.413 vs. 1.397 Å for fluorine atoms) and the shortening of the C_β-C_γ bond (1.197 vs. 1.204 Å for methyl groups and 1.193 vs. 1.198 Å for fluorine atoms), favoring a greater participation of mesomeric form I.

When substitution takes place at C_α and C_γ simultaneously, the C_α-C_β and C_β-C_γ bond lengths are intermediates between those corresponding to α- and γ-monosubstituted derivatives.

The corresponding charge distributions (see Figure 4) clearly indicate that the behavior of disubstituted propargyl cation derivatives is consistent with that of monosubstituted derivatives, presented in the previous section.

The two trisubstituted derivatives present a shortening of the C_α-C_β and a lengthening of the C_β-C_γ bonds, relative to the α,α-disubstituted derivatives, as we would expect, since γ substitution (and the third substituent enters on this position) favors a greater participation of mesomeric form II.

IIIf cation was studied by Olah et al.[3] using ^{13}C NMR techniques. They found that the positive charge at C_α is approximately twice that at C_γ. Our results, obtained using the YPS population analysis (see Figure 5), confirm this experimental conclusion.

The relative stabilities of di- and trisubstituted propargyl cation derivatives confirm our previous discussion. For methyl

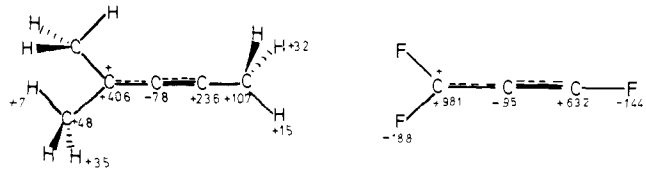


Figure 5. Charge distribution (10^{-3} electron) of trisubstituted propargyl cation derivatives.

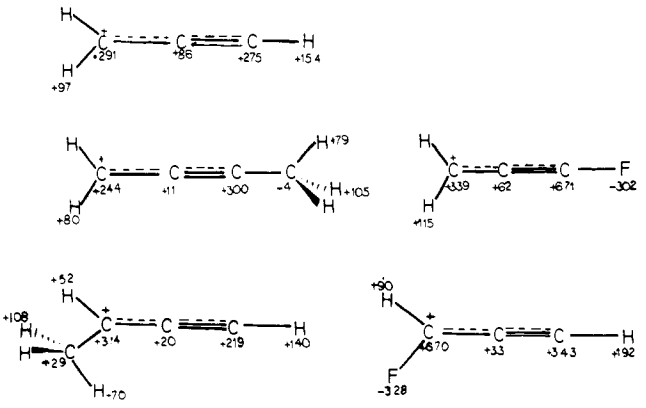


Figure 6. Charge distribution (10^{-3} electron) of propargyl cation and its monosubstituted derivatives, obtained using YPS population analysis and a 4-31G basis set.

substituents, the α,γ-disubstituted derivative is more stable than the α,α one, while for fluorine substituents the opposite situation is found.

V. Influence of the Basis Set

It has been proved[20] that the STO-3G basis gives bond lengths which are usually too long (on the order of 0.02 Å) relative to experimental values.

As the variations in bond lengths given in Table I are, sometimes, of the same order of this mean deviation, we have investigated the influence of the basis set used on the effects studied here.

For this purpose the geometry of the propargyl cation and its F- and CH_3-monosubstituted derivatives was fully optimized using a split-valence 4-31G basis set.[21] This geometry optimization was subject to the same restrictions indicated in section II. The corresponding optimized parameters are shown in Table IV. The trends found at the STO-3G level still hold at the 4-31G level and therefore our previous conclusions remain. This fact is not too surprising since it can be expected that trends are less affected by the errors introduced by the basis set used than absolute values.

The charge distribution (see Figure 6) is quite similar to the one obtained with a STO-3G basis, confirming the fact that YSP population analysis is not sensitive to the basis set used. The small deviations observed are due to the little geometrical variations introduced by the new basis.

VI. Conclusions

From our results we can conclude that progressive α substitution in alkynyl cations favors a larger contribution of mesomeric form I. γ substitution, on the contrary, increases the participation of mesomeric form II. These effects can be produced by substituents that (1) withdraw σ electrons from the substituted carbon; (2) donate π charge to the $2pC_\beta$ orbital.

α-Substituted derivatives are more stable than γ ones when the substituent is one of the first kind (fluorine). For the second type of substituents the γ-substituted derivative is the most stable one.

In the trimethyl-substituted derivative, our results agree with experimental evidence that mesomeric forms I and II participate in a ratio of about 2:1.

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