# Linear Bending in Propynyl Cation, Allene, and Propyne Systems: do they have Flexible Structures? An *ab initio* 4 -31 + G Molecular Orbital Study

**Juan Andrés, Reman Cardenas, and Orlando Tapia** *

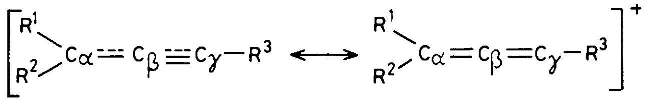
*Department of Molecular Biology, Swedish University of Agricultural Sciences, Uppsala Biomedical Centre, Box 590, S-75124 Uppsala, Sweden*

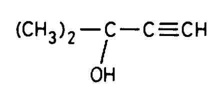
The linear bending of propyne, allene, and propynyl cation structures has been studied with SCF MO procedures. *Ab initio* gradient calculations are used to determine structural information. Force constants are evaluated. The results show fairly flexible structures under linear bending. The propynyl cation has a marked anisotropy; the out-plane linear bending (the plane is defined by the $CH_2$ group) is the softer mode. The electronic structure for the cation presents a fairly strong *nucleophilic* centre at the $C_\beta$ atom. Interestingly, 10° bending of propyne or allene does not require more than 1.10 kcal mol$^{-1}$. For the alkynyl cation 0.6 kcal mol$^{-1}$ is required. The theoretical results show that linear bending makes an integral part of the reactivity properties of all these species.

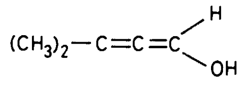
Recent *ab initio*[1] and semi-empirical[2] studies of minimum-energy profiles for the rate limiting step of the Meyer–Schuster reaction[3] have led to a detailed characterization of transition state (TS) structures for this reaction in aqueous and non-aqueous acid media. For non-aqueous acid media the TS structure was described as an alkynyl cation interacting with a water molecule; this water molecule results from the oxygen protonation of the substrate molecule, namely an α-acetylenic tertiary alcohol. The study of the reaction path with semi-empirical[2] and *ab initio* methods has shown a *linear bending* of the $C_\alpha C_\beta C_\gamma$ structure that occurs once the water has passed by the TS and initiates the $C_\gamma$ attack.[2,4] The results are somewhat puzzling in view of the presumed electronic structure of propargylic cations as epitomized by the resonance structures which convey the idea of a fairly stiff skeleton.[3]

As the linear bending appeared in connection with the interconversion of a protonated α-acetylenic alcohol into an allenol structure, the potential energy curves for the model compounds (2) and (3) and the associated alkynyl cation were calculated with MO procedures; semi-empirical (CNDO/2) and *ab initio* (STO-3G basic set) formalisms were employed. Both calculation schemes produced similar trends.[4] Surprisingly, all structures were fairly flexible. However, the carbocation (4) was consistently more flexible than structures (2) and (3). The flexibility was measured by the energy required to impart a fixed bend to the linear structure. Furthermore, the *ab initio* results showed an important change of the electron density at $C_\beta$. This centre is slightly positive for the linear structure; it becomes fairly negative as bending proceeds. This result is relevant in connection with the mechanistic interpretation of metal salt-catalysed interconversion of acetylenic halides or esters into the corresponding allenes.[5,6] To overcome the limitation of the minimal basis set a split-valence shell was tried. Our preliminary 4-31G basis set calculations of this alkynyl cation revealed a $C_\beta$-centre as permanently bearing an excess of electrons.

In fact, from the theoretical side the allenic structure has proven to be a most intriguing system.[6] In view of the broad interest that a proper characterization of alkynyl cation and related allene and acetylenic structures might have for a sounder understanding of their reactivity, an *ab initio* study of the model systems (5)—(7) with an extended basis set (4-31 + G)[7] is now reported. The model systems cover neutral and cationic species. For the sake of comparison we have used the same basis set throughout. We have not adjusted the carbon-centred function for the cation with exponents appropriate to cationic centres. The reason is that in alkynyl cations [*cf.* (1)] the carbon centres may be alternatively cationic ($C_\alpha$,$C_\gamma$) and anionic ($C_\beta$) in character.[4] The hypothesis behind the present study is that linear bending is closely related to the ability of the $C_\beta$-centre to become nucleophilic. This is the rationale behind the inclusion of a diffuse *s*-orbital at each carbon centre. The detection of geometrical trends in bond angles and bond lengths requires geometrical refinement where the largest residual forces on any atom in the molecule considered are not greater than *ca.* 0.005 mdyn.[8] Thus, complete geometrical optimization is carried out first until the average gradient length is taken below *ca.* 0.0002 mdyn. The potential for linear bending is calculated, the gradients of all other degrees of freedom are monitored, and force constants are calculated. The latter provide a quantitative measure of the stiffness of the linear structure.

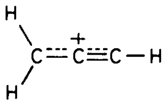

(1)


(2)


(3)

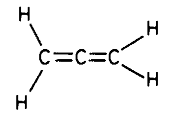
$[(CH_3)_2-C{=}C{\equiv}CH]^+$

(4)


(5)

$H_3C-C\equiv CH$

(6)


(7)

*Minimum-energy Structures.*—The 4-31 + G minimum energies for structures (5)—(7) have been determined with the optimally conjugated gradient method.[9,10] They are reported in Table 1a. As expected, they all display a linear structure for the $C_\alpha C_\beta C_\gamma$ skeleton. Effective charges derived from Mulliken's population analysis are given in Table 2.

**Table 1.** Comparative study of propyne, alkynyl cation, and allene structure. Bond lengths in Å and bond angle in degrees

| | | $C_\alpha$–$C_\beta$ | $C_\beta$–$C_\gamma$ | $C_\alpha$–H | $C_\gamma$–H | $HC_\alpha H$ |
|---|---|---|---|---|---|---|
| Propyne | 4-31 + G | 1.4598 | 1.1905 | 1.0514 | 1.0828 | 108.04 |
| | Exp[a] | 1.459 | 1.206 | 1.056 | 1.105 | 108.7 |
| | STO-3G[b] | 1.484 | 1.170 | 1.064 | 1.088 | 108.4 |
| Alkynyl cation | 4-31 + G | 1.3359 | 1.2161 | 1.0620 | 1.0758 | 117.05 |
| | STO-3G[c] | 1.36 | 1.214 | 1.091 | 1.109 | 117.8 |
| Allene | 4-31 + G | 1.2943 | 1.2943 | 1.0727 | 1.0727 | 118.26 |
| | Exp[d] | 1.308 | 1.308 | 1.087 | 1.087 | 118.2 |
| | STO-3G[b] | 1.288 | 1.288 | 1.083 | 1.083 | 116.2 |

[a] Experimental structure of the propyne: C. C. Costain, *J. Chem. Phys.*, 1958, **29**, 864. [b] STO-3G-optimized structure of propyne and allene: L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, 1971, **93**, 5339. [c] STO-3G-optimized structure of alkynyl cation: L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1976, **98**, 1. [d] Experimental structure of allene: A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, 1965, **17**, 136.

Comparisons of STO-3G and the present results with available experimental data (*cf.* Table 1) show that 4-31 + G geometrical structures agree, on the average, slightly better with experiment than the minimal basis set.

The skeleton effective charge distribution for the alkynyl cation differs significantly from those of the propyne and allene structures. The $C_\beta$-centre of the carbocation acquires a definite nucleophilic character. Interestingly, neither the propyne nor the allene charge distribution mimics the $C_\beta$-nucleophilicity of the carbocation.

*Bending Motion.*—The potential energy curves for the $C_\alpha C_\beta C_\gamma$ bending have been calculated over a range covering 20°. In this range we have observed that the gradients associated with the rest of the internal degrees of freedom are kept below $5 \times 10^{-2}$ mdyn or mdyn Å rad$^{-1}$. The alkynyl cation has two possible bendings: one corresponds to a displacement in the plane defined by the $CH_2$ structure; the other in the direction out of this plane. The results are summarized in the Figure. The potential is plotted as a function of the complementary angle $\alpha = \pi - \theta$.

The potential energy curves are seen to cluster in two classes. The out-of-plane bending of the alkynyl cation forms one of the classes by itself. The propyne, the allene in- and out-of-plane, and the alkynyl cation in-plane bending constitutes the other class. In the angular range studied the out-of-plane bending of the alkynyl cation demands rather low energy.

To quantitate the above behaviour the force constants have been calculated. For internal cross checking two methods were used.* The results are displayed in Table 2. The clustering is now quantitatively elicited. The out-of-plane linear bending for the alkynyl cation is consistently 40% lower than the ones corresponding to the allene and propyne structures. The 0.3 mdyn Å rad$^{-1}$ value for the alkynyl cation compares fairly well with CCC bending for acetone[11] (0.227 mdyn Å rad$^{-1}$).

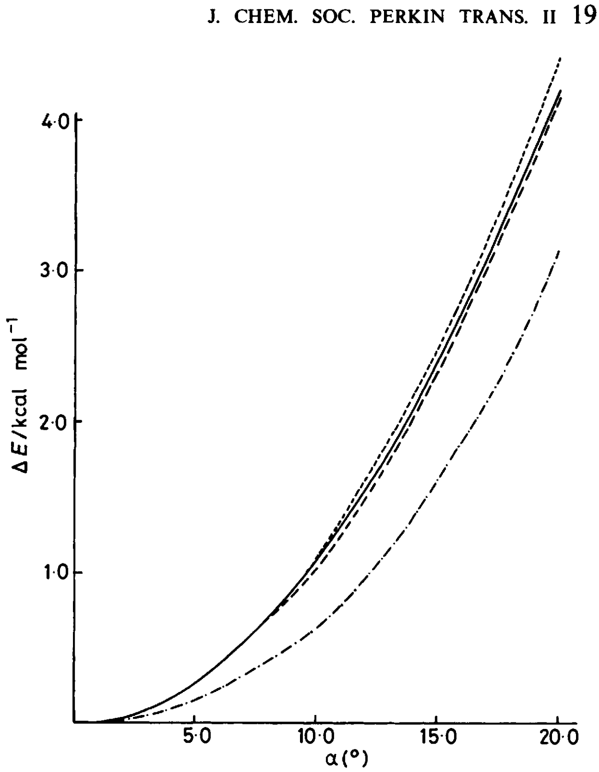


**Figure.** Potential energy curves for the linear bending of propyne cation out-of-plane (— · — · —), in-plane (— — —), propyne (——), and allene (— — —). For allene and alkynyl cation the plane is being defined by the $CH_2$ group. It is interesting to note that a 20° bending for the alkynyl cation out of the plane requires *ca.* 3 kcal mol$^{-1}$ which is an energy requirement quite easily fulfilled along a reaction pathway. In this way, as bending favours interatomic interactions with reactant partners, the energy demanded by bending can easily be supplied by intermolecular interactions. A similar argument holds for allene and propyne structures

The net atomic charges at $C_\beta$ for the three model systems show that only the alkynyl cation displays a nucleophilic centre there. On the other hand, the $C_\alpha$ and $C_\gamma$ centres of propyne and allene have strong nucleophilic character, while the alkynyl cation displays weak electrophilic centres there. By looking at the effective charges at the hydrogen centres one would expect the $H_\alpha$–$C_\alpha$ group to have increased acidity in the alkynyl cation form compared with the propyne or allene structures. It is rather clear that the resonance structures in (**1**) do not enter with equal weights in the description of the electronic structure of the alkynyl cation. They are insufficient to describe the charge distribution properly. Ionic components should also be considered.

The Mulliken population matrix elements, reduced to atoms as a function of α, are given in Table 3. A close scrutiny of the α-dependence of $P_{\alpha\beta}$ and $P_{\beta\gamma}$ shows that for the carbocation $P_{\alpha\beta}$ tends to increase slightly, while $P_{\beta\gamma}$ has the opposite trend. For the allene structure both decrease slightly, while propyne shows a slightly oscillatory trend. A hint is perhaps obtained here as far as the bonding behaviour with linear bending is concerned: the $C_\beta C_\gamma$ bond tends to be weakened, while $C_\alpha C_\beta$ behaves in the opposite fashion.

## Discussion

The flexibility of the alkynyl cation, allene, and propyne structures has been documented *via ab initio* 4-31 + G basis set MO studies. The force constants for in-plane and out-of-plane linear bendings were calculated and the charge distribution scrutinized. Since the residual forces on the atoms are sufficiently small, the information gathered on the linear bending mode has a high degree of reliability.

The electronic distribution elicited by the population analysis cannot be accounted for by the resonance structures in (**1**). The

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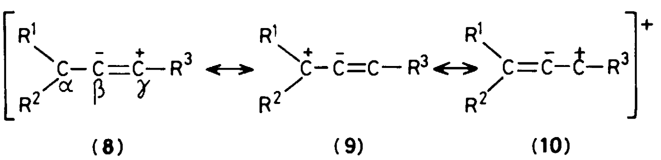
* A polynomial of fourth degree is fitted by the least-squares method, 7 and in cases 15 points around the minima have been used and the normal equations solved. The other source of force constants is the MONSTERGAUSS program.

**Table 2.** 4-31 + G net atomic charges given by a Mulliken population analysis and values of the force constants obtained for perpendicular and parallel bending

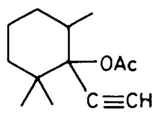
| | $\Delta Q_{C\alpha}$ | $\Delta Q_{C\beta}$ | $\Delta Q_{C\gamma}$ | $P_{\alpha\beta}$ | $P_{\beta\gamma}$ | $\Delta Q_{H\alpha}$ | $\Delta Q_{H\gamma}$ | $F_{out}{}^a$ | $F_{out}{}^b$ | $F_{in}{}^a$ | $F_{in}{}^b$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Propyne | −0.464 | −0.033 | −0.473 | 0.100 | 1.070 | 0.341 | 0.211 | 0.506 | 0.492 | 0.506 | 0.493 |
| Alkynyl cation | 0.053 | −0.207 | 0.018 | 0.404 | 0.950 | 0.472 | 0.322 | 0.310 | 0.298 | 0.482 | 0.477 |
| Allene | −0.414 | 0.041 | −0.414 | 0.620 | 0.620 | 0.197 | 0.197 | 0.497 | 0.500 | 0.502 | 0.500 |

**Table 3.** Mulliken population matrix elements reduced to atoms $P_{\alpha\beta}$ and $P_{\beta\gamma}$ and net atomic charge $Q_{C\beta}$ of the propyne, alkynyl cation, and allene structures for different values of the bending angle

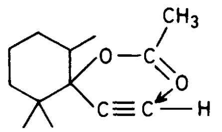
| | Propyne | | | Alkynyl cation | | | Allene | | |
|---|---|---|---|---|---|---|---|---|---|
| $\alpha$ | $P_{\alpha\beta}$ | $P_{\beta\gamma}$ | $\Delta Q_\beta$ | $P_{\alpha\beta}$ | $P_{\beta\gamma}$ | $\Delta Q_\beta$ | $P_{\alpha\beta}$ | $P_{\beta\gamma}$ | $\Delta Q_\beta$ |
| 0 | 0.097 | 1.075 | −0.033 | 0.404 | 0.950 | −0.207 | 0.622 | 0.622 | 0.041 |
| 5 | 0.105 | 1.077 | −0.033 | 0.407 | 0.948 | −0.198 | 0.617 | 0.628 | 0.040 |
| 10 | 0.127 | 1.078 | −0.035 | 0.415 | 0.940 | −0.175 | 0.603 | 0.619 | 0.040 |
| 15 | 0.150 | 1.073 | −0.040 | 0.424 | 0.928 | −0.148 | 0.585 | 0.618 | 0.039 |
| 20 | 0.172 | 1.060 | −0.047 | 0.432 | 0.915 | −0.124 | 0.509 | 0.616 | 0.035 |



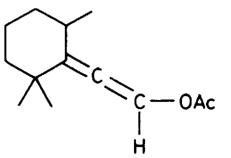
**(8)** **(9)** **(10)**



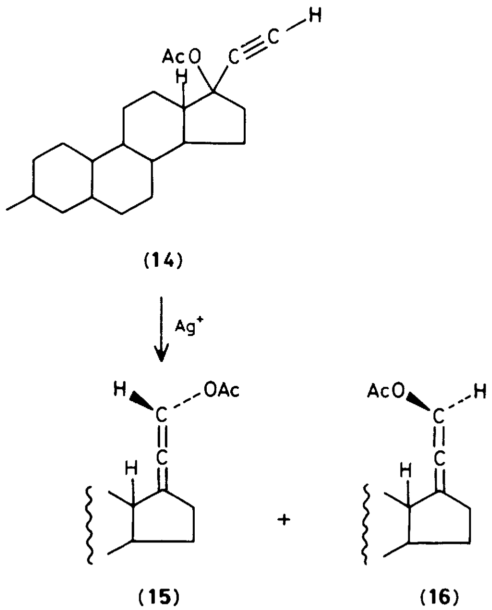
**(11)**



**(12)**



**(13)**

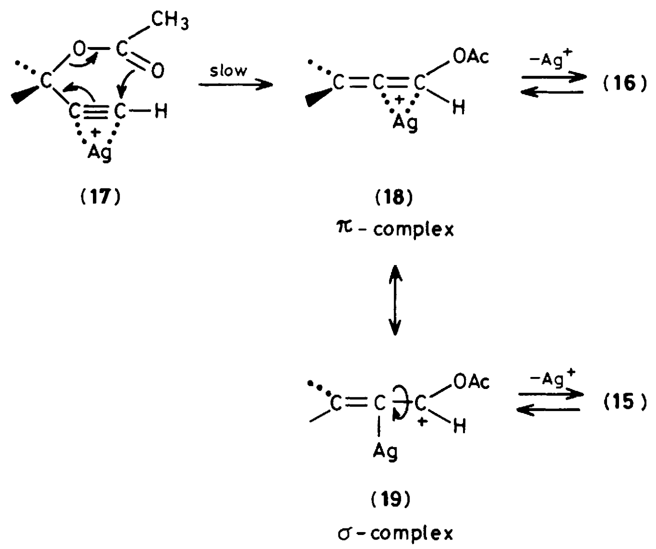


$C_\alpha$- and $C_\gamma$-centres have weak electrophilic natures, while $C_\beta$-centre is endowed with nucleophilic character. In previous work on the $[(CH_3)_2CCCH]^+$ cation with a STO-3G basis set the nucleophilic character of the $C_\beta$-centre was the result of the linear bending; the effective charge at $C_\beta$ for the linear structure was found slightly positive. This is probably a STO-3G numerical artifact. The 4-31G calculations subsequently carried out by us showed the presence of a nucleophilic centre there. The upgraded basis used in this work corroborates this result. Therefore, if a valence bond description is to be used at all, then to the resonance structure (**1**) one should add local dipole structures like (**8**)—(**10**) which describe the appearance of nucleophilic and electrophilic centres more in agreement with the MO calculations.

In the synthesis of steroidal allenes[6] the preparative method uses metal salts to catalyse the interconversion of acetylenic halides or esters into their isomeric allenes. By 1950 the catalytic influence of cuprous chloride on the equilibrium of a chloroacetylene with its isomeric allene was established. In 1956 Landor and Landor[5] postulated a *cyclic* transition state (**12**) for the reaction leading from the acetylenic ester (**11**) to the acetoxyallene (**13**). Later Benn[6] found that a silver ion-catalysed rearrangement of steroidal acetylenic esters (**14**) to the corresponding allenes (**15**) and (**16**) is an expedient preparative method. It was noticed that any consideration of the mechanism of the silver ion-catalysed rearrangement should account for the apparent lack of stereospecificity. Benn propose the Scheme to rationalize it. In fact, as the reaction proceeds by mild alkali or acid hydrolysis to unsaturated *trans*-aldehyde, these reactions may be considered as an example of a stepwise Meyer–Schuster rearrangement.[6]

It is interesting to note that in the above mechanisms the flexibility of the allene and propyne structure is *de facto* being incorporated into the argument. Furthermore, in structure (**19**) the silver ion makes a bond with the $C_\beta$-centre. This is in line with our finding of a nucleophilic centre in the alkynyl cation since one would expect structures (**18**) and (**19**) to be closely related to this cation form. The $Ag^+$ bonding might help the $sp \longrightarrow sp^2$ hybridization change. Now, if the silver cation effect is to enhance the trends found for $P_{\alpha\beta}$ and $P_{\beta\gamma}$ with linear bending, one can expect the double bond at $C_\beta C_\gamma$ to be weakened, thereby helping the rotation around this bond [*cf.* (**10**)].

From the results and discussion presented above of our pre-



Scheme.

vious work on the mechanism of the Meyer–Schuster reaction it can be concluded that the flexibility of the alkynyl cation makes an integral part of its reactivity properties. Moreover, the allene- and propyne-like fragments share this property, although they seem to be 60% stiffer than the corresponding alkynyl cation. In this connection, it can be said that one of the intriguing features of the allenic structure as voiced by Benn can be traced back to this theoretically unexpected flexibility to linear bending and, when a related alkynyl-like cation appears during the reaction, to the development of a nucleophilic centre at the central carbon atom. These factors endow these structures with special reactivity properties.

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