Theoret. Chim. Acta (Berl.) 53, 337–343 (1979)

THEORETICA CHIMICA ACTA

Structure and Charge Distribution of Some Alkynoyl Cations

A Theoretical Study

Otilia Mó and Manuel Yáñez

Departmento de Química Física y Química Cuántica, Centro Coordinado CSIC-UAM,
Facultad de Ciencias C-XIV, Universidad Autónoma de Madrid,
Cantoblanco, Madrid-34, Spain

We have performed *ab initio* calculations to determine the structure and charge distribution of some alkynoyl cations and their parent alkynoyl fluorides. We have used Mulliken population analysis and a new technique developed by Yáñez, Stewart and Pople. Our results indicate that the mesomeric form $O^+{\equiv}C_\alpha{-}C_\beta{\equiv}C_\gamma{-}R$ is one of the most important contributors to the structure of these cations, in agreement with experimental conclusions. We have also found that the participation of mesomeric form $O{=}C_\alpha{=}C_\beta{=}C_\gamma^+{-}R$ is not negligible and increases with γ-substitution. In the 3-phenylpropynoyl cation substantial delocalization of charge into the phenyl group occurs. Calculations from YSP population analysis are in good agreement with experimental evidence.

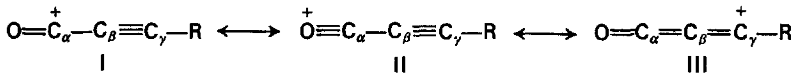
Key words: Population analysis of alkynoyl cations – Alkynoyl cations – Alkynoyl fluorides

1. Introduction

The structure and stability of vinyl and related cations is of considerable interest to the chemist since it has been proved that they are intermediates in the electrophilic additions to alkynes [1] and in the solvolysis reactions of vinyl halides [2, 5] and vinyl triflates [5, 6]. There is a considerable number of experimental studies of carbocations [7] but little is known of their structures, and most of this information comes from theoretical work [8].

Recently, proton and ^{13}C NMR spectroscopy became one of the most important experimental tools to probe the structure and charge distribution of carbocations [9] as it has been proved [10] that chemical shifts do reflect the trend of charge densities on carbon atoms of similar hybridization and substitution. One of the

0040–5744/79/0053/0337/$01.40



$$\underset{\text{I}}{O{=}\overset{+}{C}_\alpha{-}C_\beta{\equiv}C_\gamma{-}R} \longleftrightarrow \underset{\text{II}}{\overset{+}{O}{\equiv}C_\alpha{-}C_\beta{\equiv}C_\gamma{-}R} \longleftrightarrow \underset{\text{III}}{O{=}C_\alpha{=}C_\beta{=}\overset{+}{C}_\gamma{-}R}$$

Fig. 1. Mesomeric forms of alkynoyl cations

applications of this technique [11] dealt with the study of alkynylcarbenium ions and alkynoyl cations.

Alkynoyl cations were prepared (from their parent alkynoyl fluorides) and studied for the first time by Olah *et al.* [11]. These ions present an interesting structural problem: the relative importance of the mesomeric vinylic forms I, II and III (see Fig. 1) on their structure and stability.

Structure and charge distribution of some of these cations have been studied using semiempirical methods [12]. In this paper we present an *ab initio* study, using an STO-3G minimal basis set [13] of some alkynoyl cations and their parent alkynoyl fluorides. This will permit us to analyze the relative contribution of the three different mesomeric forms to the structure of this type of cation. We have also analyzed the influence of the substituents on the contribution of each particular form.

2. Calculations

We have carried out a STO-3G minimal basis set geometry optimization of propynoyl (IVa), but-2-ynoyl (IVb), 3-fluoropropynoyl (IVc) and 3-phenylpropynoyl (IVd) cations (see Fig. 2) and their corresponding parent alkynoyl fluorides (Va–Vc), except 3-phenylpropynoyl fluoride.

In the optimization process we have adopted the following restrictions: In the but-2-ynoyl cation (IVb) and but-2-ynoyl fluoride (Vb) the CH_3 group was kept unchanged, assuming local C_{3v} symmetry with the HCH angles equal to 109.47 degrees and the CH bond lengths equal to 1.10 Å. In the 3-phenylpropynoyl cation (IVd) the aromatic ring was also kept unchanged, assuming a regular ring with CC and CH bond lengths equal to 1.397 Å and 1.084 Å, respectively.

With these exceptions all the remaining geometrical parameters were optimized according to the following scheme, in order to save computation time:

a) Optimization of the C—C bond lengths
b) Optimization of the C—R bond lengths

IV a, R = H
b, R = CH_3
c, R = F
d, R = Ph

V a, R = H
b, R = CH_3
c, R = F

Fig. 2. Alkynoyl cations and their parent alkynoyl fluorides included in this study

c) Optimization of the C—O bond length (and the C—C—O angle, in the case of neutral molecules)
d) Optimization of the C—F bond length and the C—C—F angle, only for neutral molecules
e) Steps a), b), c) and d) were repeated until changes in the total energy were less than 10^{-5} a.u. for variations of ±0.005 Å in the bond lengths and 0.2 degrees in the bond angles. For the 3-phenylpropynoyl cation this process was executed only once, to save computing time.

Once the optimized geometry was obtained we carried out a Mulliken population analysis on all the systems studied.

Very recently, Yáñez, Stewart and Pople [14] have developed a new partition technique based in the use of spherical density basis functions that do not present the limitations of the Mulliken populations analysis [15] in the sense that the charge distribution obtained is quite insensitive to the basis set used in the SCF calculation. This technique gave good results [14] in the population analysis of neutral molecules. We have applied this method (which will be referred to hereafter as YSP population analysis), using the standard density basis functions defined in Ref. [14], to obtain the charge distribution of alkynoyl cations and alkynoyl fluorides to check the reliability of this partition technique applied to charged systems.

3. Structure and Charge Distribution

We present in Table 1 the optimized geometry of the alkynoyl cations and their parent alkynoyl fluorides, included in this study.

The only experimental structure found in the literature was that of alkynoyl fluoride [16]. The agreement between our results and the experimental ones is not very good, but the experimental structure was obtained by introducing several assumptions (C≡C, C=O, and C—H bond lengths) due to the limited isotopic data available, which prevents that structure from being very accurate.

In all cases there is a drastic shortening of the CO bond length in going from the neutral molecule to the cation and there is also a shortening of the C_α—C_β bond length and an increase in the length of the C_β—C_γ bond. This indicates that the oxonium form II is one of the most important mesomeric contributors, in agreement with the ^{13}C nmr study of Olah *et al.* [11], who conclude that form II is the predominant one in order to explain the surprising fact that the α carbon in the IVa and IVb cations is substantially shielded with respect to their precursors Va and Vb. However, our results indicate that form III cannot be neglected, and somewhat qualify the conclusions of these authors.

In Fig. 3 we present the charge distribution of all systems studied here, using the Mulliken and YSP population analyses.

Mulliken population analysis indicates that the positive charge on C_α in the cation is greater than in the neutral molecule. YSP population analysis gives a smaller charge in the cation than in the neutral molecule. The difference in the charge on

Table 1. Geometrical parameters for alkynoyl cations and their parent alkynoyl fluorides in the conformation of minimal energy

	Alkynoyl cations				Alkynoyl fluorides		
	IVa	IVb	IVc	IVd	Va	Vb	Vc
Bond lengths (Å)							
C_α—C_β	1.377	1.361	1.362	1.349	1.483 (1.454)	1.479	1.480
C_β—C_γ	1.193	1.200	1.197	1.207	1.174 (1.209)	1.176	1.174
C_γ—R	1.092	1.487	1.282	1.429	1.100 (1.055)	1.479	1.314
C_α—O	1.149	1.151	1.150	1.155	1.216 (1.181)	1.214	1.216
C_α—F					1.355 (1.331)	1.359	1.356
Bond Angles (degrees)							
C_β—C_α—O					125.9 (127.2)	128.0	126.0
C_β—C_α—F					113.1 (109.6)	112.4	113.1
F—C_α—O					121.0 (123.1)	119.6	120.9
Energies (a.u.)	−186.27094	−224.88665	−283.72781	−413.07529	−284.55851	−323.05903	−382.01094

Experimental values in parentheses were taken from Ref. [16].

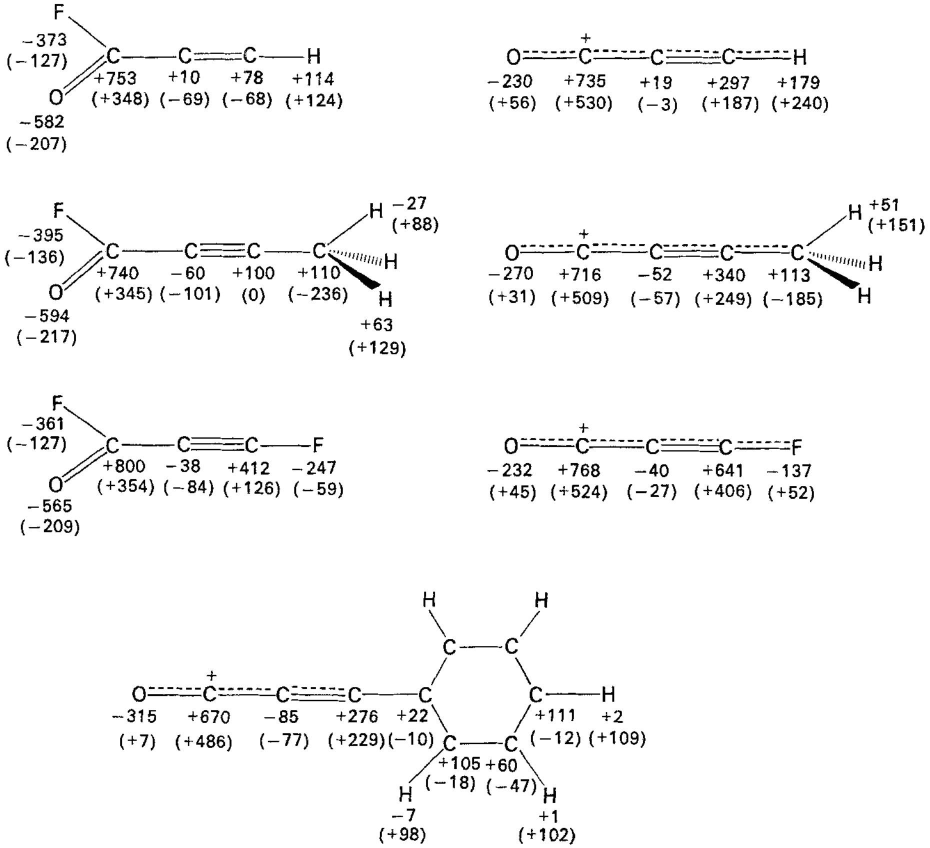


Fig. 3. Charge distribution (10^{-3} electron) of alkynoyl cations and their parent alkynoyl fluorides obtained using the YSP population analysis. Values within parentheses were obtained using Mulliken population analysis

C_α between the ion and the precursor is a little bit bigger in IVb than in IVa. Both types of population analysis indicate a considerable increase in the charge on C_γ in the cations relative to the neutral molecules. However, while Mulliken population analysis indicates that this increase is greater in IVa than in IVb, the YSP population analysis yields the opposite trend.

The charge at the oxygen atom is about the same for all cations. In going from the neutral molecule to the cation, this charge decreases considerably indicating, once again, that the mesomeric form II is one of the most important contributors to the structure of these cations.

Although no experimental data are yet available for the IVc cation, our results indicate that the general behaviour discussed for IVa and IVb could be extended to this case. The most important difference with the previous cases is that the C_γ charge is particularly large in IVc due to the expected polarization of the σ C—F bond.

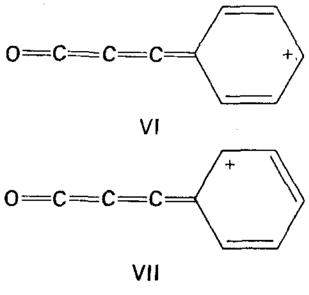


Fig. 4. Additional mesomeric forms of 3-phenylpropynoyl cation

Our results for the 3-phenylpropynoyl cation (IVd) show no substantial changes in the charges at C_α, C_β or C_γ with respect to the other cations, although there is a considerable delocalization of charge into the *ortho* and *para* positions of the aromatic ring, indicating that in this particular ion mesomeric forms VI and VII (see Fig. 4) must be included in the description of its structure, in agreement with experimental conclusions [11].

4. Influence of the Substituents

From the values of the geometrical parameters presented in Table 1, it is evident that shortening of the C_α—C_β and lengthening of the C_β—C_γ bonds are emphasized when the γ-hydrogen is substituted by fluorine atoms or methyl groups.

This indicates that γ-substitution favors a larger contribution of form III. It is clear that a different process must be responsible for this effect, in each case, given the different nature of the substituents.

Fluorine substitution produces a substantial increase of the C_γ charge (see Fig. 3) favouring a greater participation of form III (see Fig. 1). Therefore, in this case, is the withdrawal of σ-electrons from the C_γ atom that increases the contribution of form III. When the substituent is a methyl group there is no substantial increase of the C_γ charge, and the effect must be of hyperconjugative type. In Table 2 we present the electron charge density in the p_y orbitals (perpendicular to the molecular plane) for the IVa, IVb and IVd cations. We can see that a donation of electrons into the $2p$ orbitals at C_α and C_β (with the corresponding increase of their electron density) occurs when the γ-H is substituted by a —CH_3 group. Again, this increases the contribution of form III.

Of course, this effect must be stronger when the substituent is a phenyl group.

Table 2. Electron density in the p_y orbital of propynoyl (IVa), 2-but-ynoyl (IVb) and 3-phenylpropynoyl (IVd) cations

Cation	C_α	C_β	C_γ
IVa	0.753	1.100	0.786
IVb	0.762	1.126	0.773
IVd	0.780	1.163	0.773

Table 2 shows that in the case of IVd the increase of the $2p_y$ charge density at C_α and C_β is bigger than in IVb, corresponding to a shorter C_α—C_β and a longer C_β—C_γ bond length and a greater participation of form III.

5. Conclusions

From our results we can conclude that oxonium forms I and II are the predominant mesomeric contributors to the structure of alkynoyl cations, in agreement with the results of cmr studies. We have also observed that the participation of form III is not negligible and that its relative importance increases when the γ-hydrogen is replaced by substituents that either withdraw σ-electrons from the C_γ atom or donate π charge which migrates to C_α and C_β. In the case of the 3-phenylpropynoyl cation, an important delocalization of charge takes place in the ring, making participation of mesomeric forms VI and VII also important.

Finally, YSP population analysis seems to be useful to calculate charge distributions in cations, giving values which are consistent with structural experimental evidences.

Acknowledgements. All calculations were performed on the IBM 360/65 computer at the UAM/IBM Center, Madrid. We would like to thank one of our referees for pointing out an error in the manuscript.

References

1. Yates, K., Schmid, G. H., Regulski, T. W., Garrat, D. G., Leung, H. W., McDonald, R.: J. Am. Chem. Soc. **95**, 160 (1973)
2. Rappoport, Z., Bassler, T., Hanack, M.: J. Am. Chem. Soc. **92**, 4985 (1970)
3. Schiavelli, M. D., Hixon, S. C., Moran, H. W.: J. Am. Chem. Soc. **92**, 1082 (1970)
4. Schiavelli, M. D., Hixon, S. C., Moran, H. W., Boswell, C. J.: J. Am. Chem. Soc. **93**, 6989 (1971)
5. Rappoport, Z., Houminer, Y.: J. Chem. Soc. Perkin Trans. **2**, 1506 (1973)
6. Stang, P. J., Dueber, T. E.: J. Am. Chem. Soc. **95**, 2686 (1973)
7. Richey, H. G., Jr., Richey, J. M., in: Carbonium ions, Vol. 2, G. A. Olah and P. v.R. Schleyer, Eds. New York: Interscience 1970; Modena, G., Tonellato, U.: Advan. Phys. Org. Chem. **9**, 185 (1971); Stang, P. J.: Progr. Phys. Org. Chem. **10**, 276 (1973), and Refs. therein
8. Radom, L., Pople, J. A., Schleyer, P. v.R.: J. Am. Chem. Soc. **94**, 5935 (1972); Radom, L., Hariharan, P. C., Pople, J. A., Schleyer, P. v.R.: J. Am. Chem. Soc. **95**, 6531 (1973); **98**, 10 (1976); Apeloig, Y., Schleyer, P. v.R., Pople, J. A.: J. Org. Chem. **42**, 3004 (1977)
9. Olah, G. A., Pittman, C. U., Jr., Advan. Phys. Org. Chem. **4**, 305 (1966)
10. Olah, G. A., Westerman, P. W.: J. Am. Chem. Soc. **95**, 7530 (1973)
11. Olah, G. A., Spear, R. J., Westerman, P. W., Denis, J. M.: J. Am. Chem. Soc. **96**, 5855 (1974)
12. Pittman, C. U., Jr., Kim, B., Quock Ng, Y., Kispert, L. D.: J. Chem. Soc. Perkin Trans. **2**, 621 (1976)
13. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
14. Yáñez, M., Stewart, R. F., Pople, J. A.: Acta Cryst. **A34**, 641 (1978)
15. Politzer, P., Mulliken, R. S.: J. Chem. Phys. **55**, 5135 (1971)
16. Davis, R. W., Gerry, M. C. L.: J. Mol. Spectry. **57**, 118 (1975)

Received November 8, 1978/March 12, 1979