7414 J. Am. Chem. Soc. 1982, 104, 7414-7416

Electron Transmission Study of the Splitting of the π^* Molecular Orbitals of Angle-Strained Cyclic Acetylenes: Implications for the Electrophilicity of Alkynes

Lily Ng,[‡] Kenneth D. Jordan,*[†,‡] Adolf Krebs,* and Wolfgang Rüger

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, and Institut für Organische Chemie und Biochemie, Universität Hamburg, 2000 Hamburg, Germany. *Received March 25, 1982*

Abstract: Electron transmission spectroscopy was employed to determine the vertical electron affinities of 2-butyne, di-*tert*-butylacetylene, cyclooctyne, and 3,3,6,6-tetramethyl-1-thiacycloheptyne. The in-plane π^* orbital of the cyclic compounds was found to be much lower in energy than the π^* orbital of the linear compounds. The implication of this finding for the electrophilicity of alkynes is discussed.

Knowledge of the variations with geometry of the energies of the filled and unfilled orbitals of molecules is valuable for understanding a wide range of molecular properties.[1] In particular, such information is important for extending the applicability of frontier molecular orbital models of chemical reactivity.[2,3] For example, Houk and co-workers[2] have emphasized that alkynes may be more electrophilic than alkenes due to the greater ease of molecular distortion and the concomitant lowering of the energy of the lowest unoccupied molecular orbital (LUMO) in alkynes. In this picture the electrophilicity of benzyne, an important intermediate in several reactions, is due[2] to its "prebent" alkyne moiety and associated low-energy LUMO. The motivation for the present study is to provide *direct* experimental data on the variation of the π^* orbital energies of alkynes with the bending from linearity.

Experimental Section

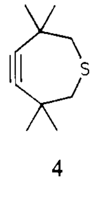
In the present investigation the technique of electron transmission spectroscopy (ETS)[6-8] is utilized to determine the vertical electron affinities (EA's) (which, in the context of Koopmans' theorem, may be associated with the energies of the unfilled orbitals) of 2-butyne (**1**), di-*tert*-butylacetylene (**2**), cyclooctyne (**3**),[9] and 3,3,6,6-tetramethyl-1-thiacycloheptyne (**4**).[10]

$H_3C—C\equiv C—CH_3$

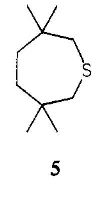
1

2

3



4



5

In the latter two compounds the angle α, which measures the deviation of the C—C≡C group from linearity, is 21.5 and 34.2°, respectively.[11,12]

In the format of ETS employed here we report the derivative of the current of a monoenergetic electron beam transmitted through the vapor of the compound of interest as a function of the impact energy. We associate the vertical electron affinities with the most probable electron attachment energies, which in the derivative spectra[7] correspond to the midpoints between the dips and the peaks. The fwhm resolution is better than 0.05 eV, and (except in the case of overlapping peaks) the absolute EA's should be accurate to ±0.05 eV.[13,14]

Table I. Vertical Electron Affinities (eV)

2-butyne	−3.43	3,3,6,6-tetramethyl-1-thiacycloheptyne	−1.16, −2.82
di-*tert*-butylacetylene	−3.10	3,3,6,6-tetramethyl-1-thiacycloheptane	−2.8 eV
cyclooctyne	−2.18, −3.28		

Results and Discussion

In Figure 1 we report the ET spectra of compounds **2**–**4**. The vertical EA's are indicated by the vertical lines in the figure. Di-*tert*-butylacetylene has a single low-energy anion state at 3.10 eV, which we assign to the degenerate π^* anion. The ET spectrum of 2-butyne is similar to that of di-*tert*-butylacetylene except that the anion is less stable, appearing at 3.43 eV, in good agreement with the 3.6-eV value obtained from the trapped electron method.[15]

[†] Camille and Henry Dreyfus Teacher–Scholar.

[‡] University of Pittsburgh.

(1) The variations of orbital energies with various distortions in simple molecules are described by the Mulliken-Walsh rules. For an excellent recent review see R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, **74**, 127 (1974).

(2) (a) R. W. Strozier, P. Caramella, and K. N. Houk, *J. Am. Chem. Soc.*, **101**, 1340 (1979); (b) N. G. Rondan, L. N. Domelsmith, K. N. Houk, A. T. Bowne, and R. H. Levin, *Tetrahedron Lett.* 3237 (1979).

(3) E. M. Burgess and C. L. Liotta, *J. Org. Chem.*, **46** 1703 (1981); F. Fukui, "Theory of Orientation and Stereoselection", Springer-Verlag, Heidelberg, 1979.

(4) E. Batich, O. Ermer, E. Heilbronner, and J. R. Wiseman, *Angew. Chem.*, **85**, 302 (1973); H. Schmidt, A. Schweig, and A. Krebs, *Tetrahedron. Lett.*, 1471 (1974).

(5) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967.

(6) L. Sanche and G. J. Schulz, *Phys. Rev. A* **5**, 1672 (1972).

(7) K. D. Jordan and P. D. Burrow, *Acc. Chem. Res. 11*, 341 (1978).

(8) A. R. Johnston and P. D. Burrow, *J. Electron. Spectrosc.* and Relat. Phenom., **25**, 119 (1982).

(9) A. T. Blomquist and L. H. Liu, *J. Am. Chem. Soc.*, **75**, 2153 (1953); L. Brandsma and H. D. Verkruijsse, *Synthesis*, 290 (1978).

(10) A. Krebs and H. Kimling, *Tetrahedron Lett.*, 761 (1970); *Liebigs Ann. Chem.*, 2074 (1974).

(11) J. Haase and A. Krebs, *Z. Naturforsch., A* **26A**, 1190 (1971).

(12) J. Haase and A. Krebs, *Z. Naturforsch., A*, **27A**, 624 (1972).

(13) The energies of the features in the cross sections are calibrated by reference to either the beam zero or to the feature corresponding to the $(1s2s^2)^2S$ state of He^-.[7]

(14) A discussion of the assumptions involved in associating the neutrals EA's with the midpoints in the ET spectra is given in P. D. Burrow, J. A. Michejda, and K. D. Jordan, "Electron Transmission Spectroscopy of Selected Alternant Hydrocarbons", to be submitted for publication to *J. Chem. Phys.*

(15) D. F. Dance and I. C. Walker, *J. Chem. Soc., Faraday Trans. II, 70*, 1426.

0002-7863/82/1504-7414$01.25/0

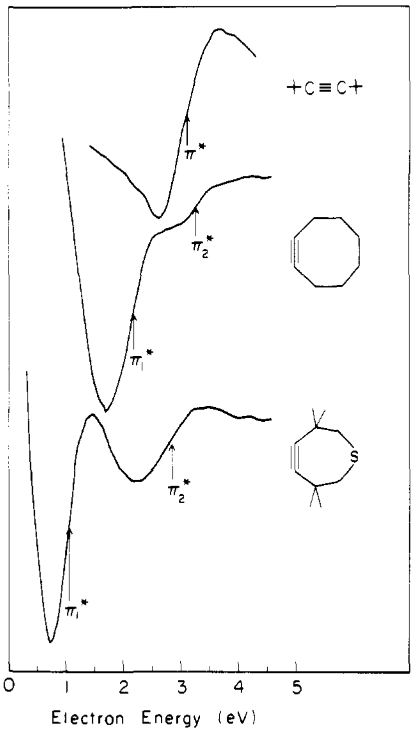


Figure 1. Derivative of transmitted current as a function of electron energy in di-*tert*-butylacetylene, 3,3,6,6-tetramethyl-1-thiacycloheptyne, and cyclooctyne.

Both of the cycloalkynes display two features in the spectra, one near 3 eV and one at lower energy. Since there is the possibility of electron captrue by the thioether portion of molecule (**4**), we have also obtained the ET spectrum of **5**, the saturated analogue to **4**. Both **4** and **5** have peaks at 2.8 eV. However, since that in **5** is much weaker and broader than in **4**, we favor the interpretation that the 2.8-eV feature in **4** is due predominantly to the acetylene portion of the molecule. A summary of our experimental results is given in Table I.

In Figure 2, we present a correlation diagram for the π and π^* orbitals as a function of C—C≡C angle for compounds **1**–**4**. The π and π^* orbital energies are taken respectively as the negatives of the vertical IP's from PES[4,16] and the vertical EA's determined here. To interpret these results, it is useful to consider the variations in the energies of the MO's of acetylene upon bending. Little change is expected for the out-of-plane ($\pi_\perp^*$ and $\pi_\perp$) orbitals, while the in-plane ($\pi_\parallel^*$ and $\pi_\parallel$) orbitals might be expected to undergo significant energy changes upon cis bending due to $3\sigma_g$–$\pi_\parallel$ and $3\sigma_u^*$–$\pi_\parallel^*$ mixing. Examination of the MO wave functions reveals that the $3\sigma_g$ orbital will undergo little variation and the $3\sigma_u^*$ orbital will drop rapidly in energy upon bending.[1] As a result, there is a strong mixing between the $\pi_\parallel^*$ and the higher lying $3\sigma_u^*$ orbitals, stabilizing the former, and little mixing between the $3\sigma_g$ and $\pi_\parallel$ orbitals.

On the basis of these considerations we assign the lower energy anion state in the two cyclic compounds to the $\pi_\parallel^*$ orbital, which occurs at 2.18 eV in **3** and 1.16 eV in **4**, showing the expected strong dependence of the LUMO energy on the degree of bending. The first anion state of **4** is 2.2 eV below that of butyne, in good agreement with theoretical predictions: STO-3G and 4-31G calculatons[2a] predict respectively a 2.7- and 2.4-eV decrease in the LUMO energy of 2-butyne upon bending of the C—C≡C angles to those in compound **4**.

The second anion states of cyclooctyne (at 3.28 eV) and **4** (at 2.82 eV) lie close in energy to the anion states of butyne and di-*tert*-butylacetylene, supporting their assignment to the electron capture into $\pi_\perp^*$. For comparison with the cycloalkynes, 2-butyne and di-*tert*-butylacetylene are more appropriate choices of linear alkynes than acetylene,[6] whose anion is much more stable, appearing at 2.6 eV. The greater stability of the *tert*-butyl species compared to the methyl-substituted compounds is attributed to the lower lying alkyl π^*-like orbitals in the former case.

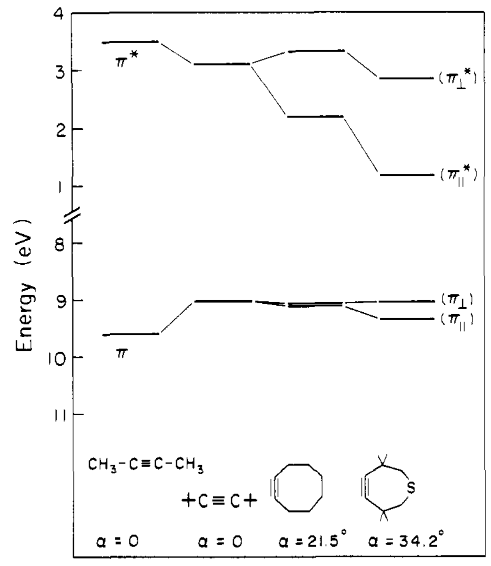


Figure 2. Correlation diagram of the vertical EA's and IP's of the linear and cyclic acetylenes.

If we fit ϵ_{LUMO} vs. α to a straight line for butyne and the two cyclic compounds and extrapolate to $\alpha = 56°$, the value in benzyne, we are led to the prediction that the LUMO of benzyne should be 4.0 eV more stable than that of butyne, in good agreement with the 4.8-eV theoretical prediction of Rondan et. al.[2b] In this consideration we have neglected changes in the EA's caused by variations in the degree of alkyl substitution. Allowing for the effects of methyl groups, we conclude that the benzyne anion is likely to be stable by 0.1–0.6 eV and that it should be observable mass spectroscopically or via photodetachment spectroscopy.

Summary

In this paper we have established that the first vertical EA of acetylenes depends strongly on the C—C≡C angle, providing support for the suggestion[2,3] that the electrophilicity of bent alkynes, such as those studied here, and benzyne derives from the presence of a low lying unfilled molecular orbital.[17] The implications are broader than this, however, as they also support the ideas that linear alkynes are more electrophilic than related alkenes because they can easily adopt a bent structure in reaction transition states.[2] In addition, since linear acetylenes adopt bent structures in their anion states[18] leading to much larger values for the adiabatic than for the vertical EA's,[19] charge transfer in the quenching of electronically excited species by acetylenes[20] may be more important than previously anticipated. Finally, we believe that bending following electron capture in acetylene enables the

---

(16) C. N. R. Rao, P. K. Basu, and M. S. Hegde, *Appl. Spectrosc. Rev.*, **15** 50 (1979).

(17) Additional support for this picture is provided by electrochemical reduction experiments. Although neither 3,3,8,8-tetramethylcyclooctyne and 4,4,7,7-tetramethylcyclooctyne show any reduction wave up to -3.0 V vs. SCE (DMF, 0.1 M (n-$C_3H_7)_4NClO_4$, working electrode mercury), compound **4** exhibits an irreversible reduction wave at -2.93 V. The corresponding alkene was not reduced under these conditions.

(18) Calculations show that following electron capture, acetylene may distort to either cis or trans structures with the trans form being somewhat more stable; S. Y. Chan and L. Goodman, *J. Am. Chem. Soc.*, **97**, 7 (1975). The difference between the vertical and adiabatic EA's may be as large as 40 kcal/mol. N. Rondan, K. N. Houk, S. Sakai and K. D. Jordan, unpublished results.

(19) Although the vertical attachment energy of acetylene is larger than the adiabatic attachment energy, the adiabatic EA is larger than the vertical value on account of the fact that electron affinities are defined as negative when the anion states lie energetically above the ground state of the neutral molecule.

(20) W. H. Breckenridge and H. Umemoto, *J. Chem. Phys.* **75**, 699 (1981); W. H. Breckenridge and O. K. Malmin, *J. Chem. Phys.* **74**, 3307 (1981).

coupling of the $^2\Pi$ anion surfaces to the dissociative $^2\Sigma$ surface correlating with $C_2H^- + H$, which is known to be an important decay channel of the acetylene anion.[21,22]

Acknowledgment. This research was supported by the National Science Foundation, the Research Corp., and the Deutsche Forschungsgemeinschaft. We are grateful to P. D. Burrow for assistance in the design and operation of the electron transmission spectrometer and for many helpful suggestions. We also thank K. N. Houk and D. W. Pratt for helpful comments on the manuscript.

Registry No. 1, 503-17-3; **2**, 17530-24-4; **3**, 1781-78-8; **4**, 26825-18-3; **5**, 53561-47-0.

---

(21) R. Azria and F. Fiquet-Fayard, *J. Phys. (Paris)*, **33**, 663 (1972).

(22) A similar coupling between $^2\Sigma$ and $^2\Pi$ anion states has been invoked to explain the $^2\Pi$ $H_2C{=}CHCl^- \rightarrow {}^2\Sigma$ $C_2H_3 + {}^1SCl^-$ process; P. D. Burrow, A. Modelli, N. S. Chiu, and K. D. Jordan, *Chem. Phys. Lett.* **82**, 270 (1981).

Fourier Analysis of the Orbital Momentum Densities of CO, NO, and O_2

John A. Tossell,*† John H. Moore,† Michael A. Coplan,‡ Giovanni Stefani,§ and Rossana Camilloni§

Contribution from the Chemistry Department and the Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742, and Istituto di Metodologie Avanzate Inorganiche, Monterotondo Scalo, Roma, Italy.

Received November 2, 1981

Abstract: Single orbital momentum densities of CO, NO, and O_2 have been measured by (e,2e) spectroscopy and have been calculated from restricted Hartree–Fock (RHF) and split valence wave functions. The analysis of these momentum densities as position space quantities is explored by taking the Fourier transform of the momentum densities to obtain the wave function autocorrelation functions $B(r)$.

Introduction

Although the orbital description of a many-electron wave function is only an approximation, it has been found to be extremely useful for interpreting a wide variety of chemical data.[1] General methods have been developed to explain molecular shapes[2] and chemical reactivities[3] using qualitative information on orbital energies and orbital electron distributions. Information on orbital energies is readily available from photoelectron spectroscopy[4] but knowledge of orbital electron distribution or shape is more difficult to obtain. Studies of the angular distributions of photoelectrons can in principle yield further information on orbital character,[6] but the theoretical interpretation of orbital asymmetry parameters has so far been only moderately successful even for simple molecules.[7] Total electron densities can be evaluated by using X-ray and electron diffraction.[9] Although theoretical calculations have shown the need for using near-Hartree–Fock basis sets to obtain valence electron densities in good agreement with experiment,[10] it appears that correlation effects will not generally be so large as the uncertainties in the experimental data for the case of X-ray diffraction.[11] In electron diffraction, higher accuracy is obtainable but the data cannot easily be interpreted for other than diatomic molecules. In addition, diffraction techniques give information on all the electrons, not separating them by orbital.

The experimental method used in the present work—(e,2e) spectroscopy[12]—yields information about individual electron orbitals. The technique consists of high-energy electron impact ionization with complete determination of the collision kinematics. The cross section for the process can be directly related to the single-electron momentum density. To understand the data in terms of conventional orbital models, one must either recast the models in the momentum representation or transform the data into the configuration space representation. We will explore both of these routes in this paper.

The (e,2e) process is an electron knockout reaction. By measuring the momenta of the incident, scattered, and ejected electrons, one can determine the instantaneous momentum of the ejected electron from conservation considerations. By repeating the process many times, one can determine the distribution of momentum values. The momentum distribution function is called the momentum density just as the position probability function is the electron density.

From the point of view of quantum mechanics, the incident, scattered, and ejected electrons are waves which under the appropriate experimental conditions can be written as plane waves. If the bound-state total wave function can be represented by a single configuration product of one-electron wave functions

$$\Psi = A_i \Pi \psi_i \qquad (1)$$

then in the binary encounter approximation the (e,2e) cross section is

$$\sigma_{(e,2e)} = K|\langle e^{i\vec{q}\cdot\vec{r}}|\psi_k(\vec{r})\rangle|^2 \qquad (2)$$

where K is a constant and the term in brackets is the Fourier transform of the wave function for the orbital from which the

---

† Chemistry Department, University of Maryland.

‡ Institute for Physical Science and Technology, University of Maryland.

§ Instituto di Metodologie Avanzate Inorganiche.

(1) K. Wittel and S. P. McGlynn, *Chem. Rev.*, **77**, 745 (1977).

(2) J. K. Burdett, "Molecular Shapes: Theoretical Models of Inorganic Stereochemistry", Wiley-Interscience, New York, 1980.

(3) G. Klopman, Ed., "Chemical Reactivity and Reaction Paths", Wiley, New York, 1974.

(4) D. W. Turner, "Molecular Photoelectron Spectroscopy: A Handbook of the 584 Å Spectra", Wiley-Interscience, New York, 1970.

(5) M. S. Banna and D. A. Shirley, *J. Electron Spectrosc.*, **8**, 225 (1976).

(6) T. A. Carlson and C. P. Anderson, *Chem. Phys. Lett.*, 10, 561 (1971).

(7) R. M. Holmes and G. V. Marr, *J. Phys. B.*, **13**, 945 (1980).

(8) P. Coppens and E. D. Stevens, *Adv. Quantum Chem.*, **10**, 1 (1977).

(9) R. A. Bonham and M. Fink, in "Electron and Magnetization Densities in Molecules and Crystals", P. Becker, Ed., Plenum Press, New York, 1980, pp 581–631.

(10) G. DeWith and D. Feil, *Chem. Phys. Lett.*, **30**, 279 (1975).

(11) J. L. DeBoer and A. Vos, *Acta Crystallogr., Sect. B*, **35**, 1809 (1979).

(12) I. E. McCarthy and E. Weigold, *Phys. Rep.*, **27**, 275 (1976).

0002-7863/82/1504-7416$01.25/0