Electronic Structure and Photoelectron Spectrum of 1,5,9-Cyclododecatriyne

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Abstract: The photoelectron spectrum and ab initio STO-3G molecular orbital calculations on the title molecule indicate substantial interactions between the formally nonconjugated acetylenic π orbitals. A comparison of the experimental spectrum and the model calculations suggest that the preferred conformation of this molecule is a pseudochair conformation of D_3 symmetry.

Introduction

If planar, the title triyne, 1,5,9-cyclododecatriyne (**1**),[2] could experience six-electron cyclic interactions of both the in-plane and out-of-plane π bonds of the three acetylene moieties, and might exhibit homoaromaticity.[3] The molecule has a substantial barrier to isomerization to triscyclobutenabenzene,[2b] the valence isomeric molecule which would result from intramolecular cycloaddition of the three acetylenic subunits. We wish to report that the photoelectron spectrum and molecular orbital calculations on **1** suggest that the molecule exists in a quasi-chair conformation of D_3 symmetry, and any cross-ring interaction is probably destabilizing.

Photoelectron Spectrum

The He(I) photoelectron spectrum of **1** is displayed in Figure 1.[4] The first multifaceted band between 9 and 10 eV encompasses all of the acetylenic π ionizations. For comparison, 2-butyne has a vertical ionization potential of 9.56 eV,[5] and the mean energy of the first band of **1** is essentially identical with this value. The second broad band in the spectrum has an onset at 12.2 eV. The σ ionization bands of 3,5-octadiyne,[6] an acetylene with two ethyl substituents, of 1,5-cyclooctadiyne,[7] a strained species having two ethano units, and of 1,5-hexadiyne,[8] an unstrained diyne with an ethano unit, are all essentially identical in shape and position with those of **1**. This provides further examples in conformity with a rule proposed by Heilbronner et al.,[6] which says that the alkyl portions of alkyne PES are practically superimposable on those of corresponding alkanes, except for a shift to higher IP caused by the acetylene moiety.

The first band consists of several maxima, as shown more clearly in the expanded inset in Figure 1. The first maximum is at 9.13 eV, and there is a barely resolved vibrational progression of 0.11 eV. The PES of acetylenes usually show vibrational structure of 0.22 eV and weaker progressions of 0.11 eV.[5] Both of these are likely present in the first band of **1**. We assign the first vertical ionization potential as 9.24 eV, since this second vibrational band maximum more nearly matches the centroid of the first ionization band than does the first maximum. There could be a second ionization at approximately 9.3 eV.

A broad envelope with a maximum at 9.63 eV follows. The intensity of this band suggests that it encompasses several ionization events. Finally, there is a sharp maximum at 9.93 eV which could be another vertical ionization, or a higher vibrational band arising from a somewhat lower energy ionization.

A purely empirical deduction of assignments cannot be made. If the geometry of the molecule were planar, then the in-plane and out-of-plane π orbitals of the acetylene units would each split into a degenerate (e) and nondegenerate (a) set of orbitals. These are shown schematically in Figure 2. The energetic order shown in Figure 2 is the "natural" order expected if through-space[9] interaction dominated. However, through-bond[9] interactions could invert this order in the following way: for the in-plane π orbitals, the single nondegenerate orbital is of the correct symmetry to be mixed with, and to be destabilized by, the CC σ orbitals. The degenerate e set will interact less with CC σ orbitals, since the e orbitals are mainly antibonding between ethyne units, and are, therefore, only of the appropriate symmetry to be stabilized by higher lying CC σ^* orbitals.

For the out-of-plane π orbitals the situation is less clear: there are π_{CH_2} orbitals of appropriate symmetry to mix with all three π orbitals, but, for symmetry reasons which can be discerned by inspecting the six possible combinations of π_{CH_2} orbitals, the nondegenerate π orbital will be influenced more than the degenerate pair of π orbitals.

We reported earlier the dominance of through-space over through-bond interactions in octamethyl-1,3,7,9-cyclododecatetrayne,[10] and **1** should have even more pronounced tendencies in this direction owing to the better through-space overlap of the π systems in **1**. It would seem reasonable on this basis that the degenerate pairs of both in-plane and out-of-plane orbitals in **1** should be at higher energy (lower IP) than the nondegenerate orbitals, and, as shown in the next section, calculations by several techniques suggest that through-space interactions dominate in **1**.

For comparison, 1,5-hexadiyne has three nearly degenerate ionizations assigned to the out-of-plane and through-bond coupled, in-plane, ionizations, and a higher ionization potential arising from the in-plane orbital which is not through-bond coupled.[8] The strained 1,5-cyclooctadiyne has a very similar spectrum to that of 1,5-hexadiyne, but it is now the positive bonding combination of out-of-plane orbitals which is assigned to the higher energy ionization band.[7]

Molecular Orbital Calculations on 1

MINDO/3[11] was first tried to explore the relative energies of planar and nonplanar conformations of **1**. However, orbital energy orderings and ionization potentials are not reliably predicted by this technique when both through-bond and through-space mechanisms of orbital coupling are involved,[12] and in the present case the ionization potentials predicted from MINDO/3 using Koopmans' theorem[13] did not resemble the pattern observed experimentally. For that reason, calculations on several assumed geometries were carried out using ab initio

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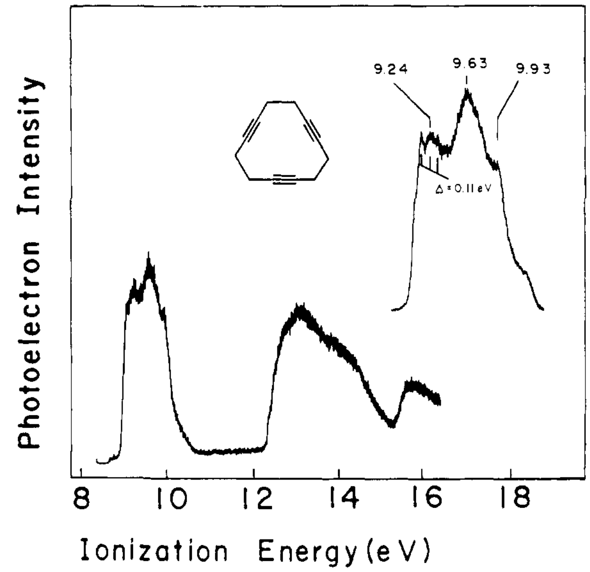

Figure 1. The photoelectron spectrum of 1,5,9-cyclodecatriyne.

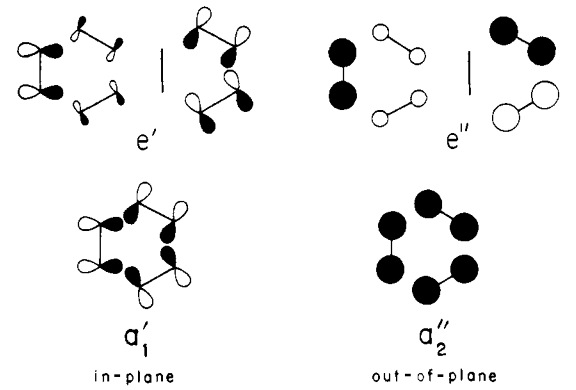

Figure 2. The in-plane (π_i) and out-of-plane (π_o) orbitals of three interacting acetylenes in a plane.

techniques with the STO-3G minimal basis set.[14] These are summarized in Figure 3.

The planar D_{3h} model was derived from experimental bond lengths for appropriate fragments and the $C_1C_2C_3$ angle of propane to set the angles at the saturated corners. To maintain planarity, this requires a 7.8° bending of each acetylene terminus. The D_3 model was based on the same bond lengths, but linear acetylenes and a regular tetrahedral angle at the saturated corners were used. Assuming a chair-like geometry, the dihedral angles shown were derived. For reference, these should be compared to the 60° dihedral angles of chair cyclohexane. Although no optimizations were carried out, it is of interest that the D_3 geometry is 16 kcal/mol more stable than the D_{3h} according to the STO-3G calculations.

The orbital energies for the six orbitals which have mainly acetylenic π character are shown in Figure 4. The values given for each orbital are calculated ionization potentials obtained by the following equation, derived earlier to fit STO-3G orbital energies to experimental ionization potentials for simple acetylenes:[10]

$$\mathrm{IP(calcd)} = 0.778(-\epsilon^{\mathrm{STO\text{-}3G}}) + 3.40$$

In the planar molecule, the "natural order" is predicted. Furthermore, the in-plane and out-of-plane orbitals are only slightly different in energy. The average of the out-of-plane π orbitals (9.59 eV) is virtually identical with that of the in-plane π orbitals (9.58 eV). There is slightly greater splitting of the out-of-plane orbitals, suggesting somewhat stronger interaction through π overlap.

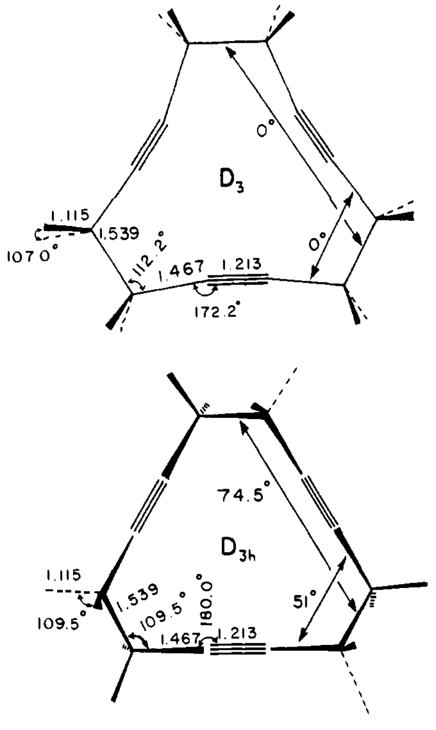

Figure 3. Model geometries used for STO-3G calculations.

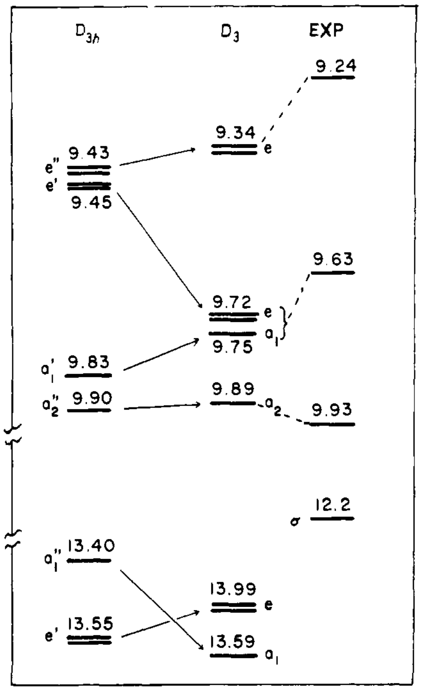

Figure 4. Corrected[10] STO-3G orbital energies for planar D_{3h} **1** and chair-like D_3 **1**, and experimental ionization potentials.

If **1** were planar, the STO-3G calculations suggest that two bands would be observed. The first would be due to four ionizations around 9.4 eV, and could be somewhat broadened due to Jahn-Teller distortion of the degenerate radical cation states formed by ionization from any of these π orbitals. A second, less intense, band encompassing two ionizations is expected at 9.8 eV for the planar molecule. There is little resemblance between this prediction and the experimental photoelectron spectrum.

The STO-3G prediction for the chair geometry is in much better agreement with the spectrum. Upon conversion of the D_{3h} planar conformation to the D_3 chair conformation, the in-plane (e′) π orbitals and the out-of-plane (e″) π orbitals of the D_{3h} conformation can mix, since they are now of the same symmetry (e) in the reduced D_3 symmetry of the chair conformation. The result of this mixing is a splitting of the nearly degenerate e′ and e″ sets in the D_{3h} conformation into two sets with a substantial separation in the D_3 conformation. The resulting positions of the e orbitals in the D_3 conformation can best be analyzed in two steps. First, imagine that the geometry is changed from the planar D_{3h} conformation to the chair D_3 conformation without allowing interaction between the two sets of π orbitals. This causes both sets of π orbitals to be stabilized because of a decrease in antibonding interactions between the three acetylene moieties. Upon allowing these two sets to interact, a stabilized set and a destabilized set are formed. These can no longer be clearly called in plane and out of plane but are mixtures of the two original sets.

For the lower energy a_1' and a_2'' orbitals of the planar conformation, the effect of changing the geometry is to decrease overlap between the acetylene units, causing them to be destabilized. Now, allowing these to mix with CH and CC σ orbitals of appropriate symmetry causes the a_2'' (out-of-plane) π orbital to be stabilized by a decrease in an antibonding interaction with lower energy σ orbitals, while the a_1' (in-plane) π orbital experiences no change in mixing with lower energy σ orbitals and remains at the same energy obtained in the first part of the analysis.

Another effect of the change in geometry from D_{3h} to D_3 is the change in the ordering of the high-lying σ orbitals of **1** as seen in Figure 4. The a_1'' σ D_{3h} orbital is derived from the antibonding combination of the ethane out-of-plane π_{CH_2} orbitals located on each ethane fragment. The three ethane fragments interact in an antibonding manner in the planar geometry. The relaxation of the geometry from D_{3h} to D_3 is essentially the same as converting an eclipsed ethane to a staggered ethane. The antibonding interactions in the a_1'' orbital are decreased, leading to stabilization. The e′ set of σ orbitals is composed of antibonding combinations of the in-plane orbitals resembling the π_{CH_2} orbitals of ethane. Upon bending, these are destabilized by mixing with lower lying e″ out-of-plane σ orbitals. The orbital energy order deduced from calculations shares only one common feature with 1,5-hexadiyne and 1,5-cyclooctadiyne studied by others:[6,7] in all three molecules, the fully bonding out-of-plane π orbital is the lowest owing to simultaneous maximal through-space bonding and minimal through-bond antibonding interactions.

The STO-3G calculations on the standard D_3 geometry predict that there should be a band at about 9.4 eV, a broader, more intense band containing three ionizations around 9.7 eV, and a less intense, one ionization band at about 9.9 eV. This prediction is in quite reasonable agreement with the experimental spectrum. We conclude that **1** has a D_3 chair-like conformation similar to the model shown in Figure 3. The largest discrepancy between the STO-3G calculation and the photoelectron spectrum of **1** lies in the first IP. This discrepancy suggests that the actual geometry may be distorted in the direction of increasing the through-space interactions between the acetylene moieties, by bending of the acetylenes, or by an outward bending which would raise the energies of both sets of e orbitals. This molecule, like others studied for potential homoaromatic character,[3] avoids what would appear to be stabilizing six-electron interactions. The origin of this phenomenon will be discussed in general elsewhere.[15]

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References and Notes

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