

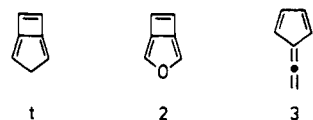
Photoelectron Spectra of 2,5-Dehydrotropylidene, 3,6-Dehydrooxepin, and Fulvenallene^{1a}

Claus Müller,^{1b} Armin Schweig,^{*1b} Walter Thiel,^{1b} Walter Grahn,^{1c}
Robert G. Bergman,^{1d} and K. Peter C. Vollhardt^{1d}

Contribution from the Fachbereich Physikalische Chemie, Universität Marburg, the Fachbereich Chemie, Universität Marburg, D-3550 Marburg/Lahn, West Germany, the Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720.
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Abstract: The He I photoelectron spectra of the title compounds are presented and interpreted chiefly by comparison with calculated data using the PERTCI method, a recent large-scale CI approach, in conjunction with semiempirical MNDO, CNDO/S, and LND0/S wave functions. The geometric structure and some aspects of the electronic structure of 3,6-dehydrooxepin are discussed on the base of MNDO data.

We wish to report the photoelectron spectra of bicyclo[3.2.0]hepta-1,4,6-triene (2,5-dehydrotropylidene, **1**),² 3-oxabicyclo[3.2.0]hepta-1,4,6-triene (3,6-dehydrooxepin, "furocyclobutadiene", **2**),³ and fulvenallene (**3**),² and some



results on the electronic structure of these compounds, especially of **2**.

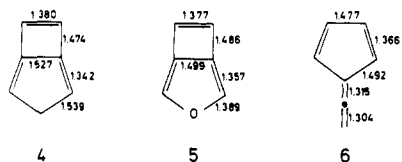
Results and Discussion

Figures 1–3 display the He I photoelectron spectra of the reactive species **1**–**3**, respectively. Figure 4 exhibits bands 1 and 2 of the spectrum of Figure 1 on an expanded scale.

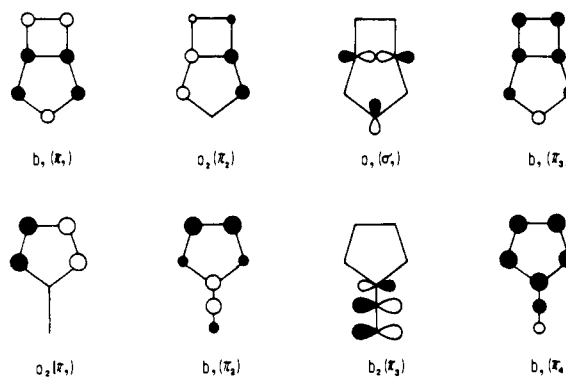
Both Koopmans and PERTCI⁴ calculations⁵ using MNDO,⁶ CNDO/S,⁷ and LND0/S⁸ (where possible at present⁹) wave functions lead to consistent assignments for the first three bands of **1** (²B₁(π₁), ²A₂(π₂), and ²A₁(σ₁); cf. Figure 5), **2** (²B₁(π₁), ²A₂(π₂), and ²A₁(σ₁); cf. Figure 6), and **3** (²A₂(π₁), ²B₁(π₂), and ²B₂(π₃); cf. Figure 7), respectively.

From large-scale tests on the quality of MNDO and CNDO/S ionization potentials of π systems it is known¹⁰ that the CNDO/S σ ionizations often occur at energies that are too low. Taking account of this trend band 4 in each spectrum is probably a π ionization (²B₁(π₃) for **1** and **2** and ²B₁(π₄) for **3**; cf. the respective Figures 5–7).

The theoretical data of Figures 5–7 have been obtained for MNDO optimized geometries (see 4–6). The orbitals from



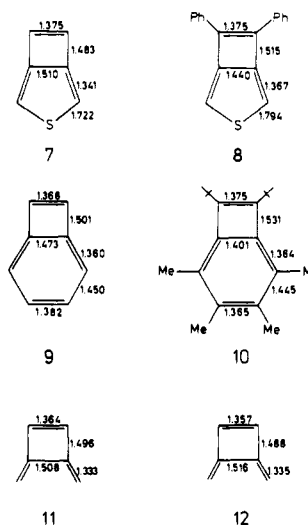
which an electron is ejected in the Koopmans ionization processes are schematically depicted below (for **1** and **2** on top and **3** on bottom). An independent qualitative argument for the sequence of the first two ionizations of **1** and **2** is based on the nodal structure of the respective orbitals. Accordingly, only the ²B₁(π₁) ionization is anticipated to be markedly shifted to lower energy on replacing the methylene grouping in the



five-membered ring by an oxygen atom, in agreement with the measurements.

After the present work was completed the PE spectrum of fulvenallene was reported and assigned following alternative procedures.¹¹ Both the measured vertical ionization potentials and the assignments are in perfect agreement with the present study.

The reliability of the calculated MNDO structures **4** and **5** has been tested on the related systems 3-thia bicyclo[3.2.0]-1,4,6-triene ("thienocyclobutadiene"), bicyclo[4.2.0]octa-1,3,5,7-tetraene ("benzocyclobutadiene"), and 3,4-dimethylenecyclobutene.¹² Comparison of the calculated structures of these systems¹³ (see **7**, **9**, and **11**) and of measured^{14–16} structures (see **8**, **10**, and **12**; note substituents in **8** and **10**)



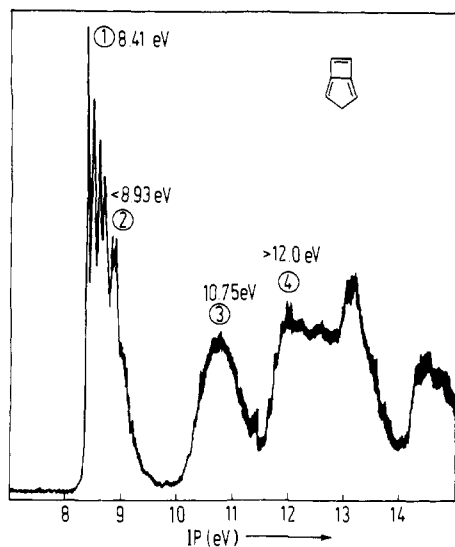


Figure 1. He I photoelectron spectrum of bicyclo[3.2.0]hepta-1,4,6-triene (2,5-dehydrotropylidene). The numbers associated with each band are the respective vertical ionization potentials (VIPs).

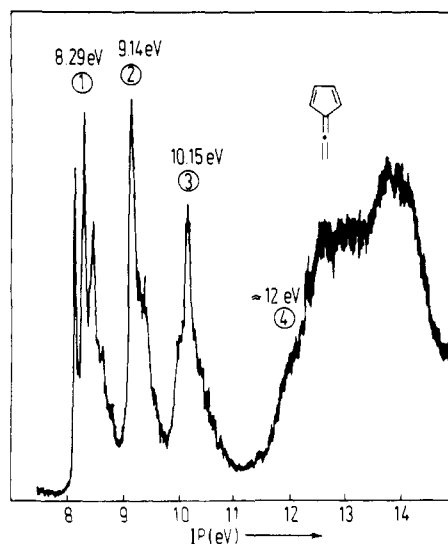


Figure 3. He I photoelectron spectrum of fulvenallene. The numbers associated with each band are the respective VIPs.

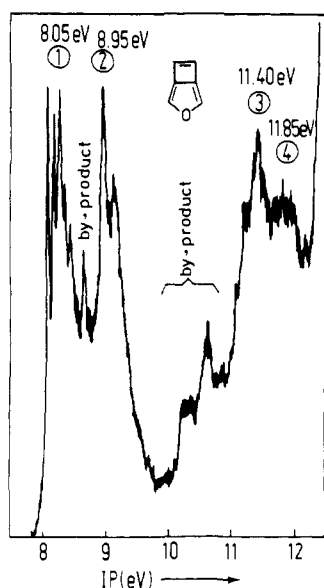
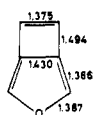


Figure 2. He I photoelectron spectrum of 3-oxabicyclo[3.2.0]hepta-1,4,6-triene (3,6-dehydrooxepin). The numbers associated with each band are the respective VIPs.

reveal a remarkably good agreement between the theoretical and experimental perimeter bond lengths which alternate strongly. On the other hand, the observed length of the central "backbone" bond in **8**¹⁴ and **10**¹⁵ is about 0.07 Å shorter than the calculated one in **7** and **9**.

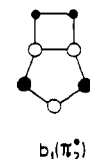
To study this effect further, the structure of **2** was reoptimized keeping the length of the central bond fixed at 1.430 Å (i.e., reducing the optimized value by 0.07 Å; see **13** below); analogous calculations were carried out at 1.400 and 1.370 Å. Comparison of the data shows that this deformation has little effect on the perimeter bond lengths (less than 0.01 Å), the ionization potentials (less than 0.2 eV), and the total energies



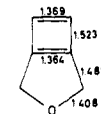
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(increase of 2.1, 4.6, and 8.2 kcal/mol, respectively). The properties of **2** thus seem to be determined mainly by the π conjugation along the perimeter, and much less by the length of the central bond.

Even at 1.370 Å, the π bond order of the central bond (0.458) is smaller than that of the corresponding bond in furan (0.501). A species with a full central π bond (π bond order 1.000) corresponds to a doubly excited state of **2**, where two electrons have been promoted from the $a_2(\pi_2)$ orbital (depicted above) to the $b_1(\pi_2^*)$ orbital (shown below). The corre-

 $b_1(\pi_2^*)$

sponding structure was optimized by MNDO (see **14** below) and lies 150 kcal/mol above the ground-state structure



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(MNDO-PERTCI ionizations at 5.12 and 9.19 eV). Such an excited configuration contains a true cyclobutadiene subunit, but it is so high in energy that it does not contribute significantly to the ground state of **2**.

Experimental Section

The spectra of the reactive species **1**–**3** were recorded on a Perkin-Elmer PS16/18 spectrometer. The materials were prepared according to the following procedures.

Bicyclo[3.2.0]hepta-1,4,6-triene and Fulvenallene. *trans*-1,2-Diethynylcyclopropane was prepared and pyrolyzed in a vacuum flow system as described by D'Amore.^{2,17} The pyrolysis mixture was separated by preparative GLC (Perkin-Elmer F-21, 5% SE-30 on Chromosorb G AW-DMCS, 3.6 m \times 3/8 in., 80 °C, 150 mL/min N₂). The products were isolated and transferred in traps which were cooled with acetone/dry ice and could be closed by stopcocks and mounted to the inlet line of the PE spectrometer. The purity of the products was checked by ¹H NMR spectroscopy (solvent CDCl₃). The NMR data obtained correspond to those reported by D'Amore.² In the case of bicyclo[3.2.0]hepta-1,4,6-triene, which is very unstable in pure form,

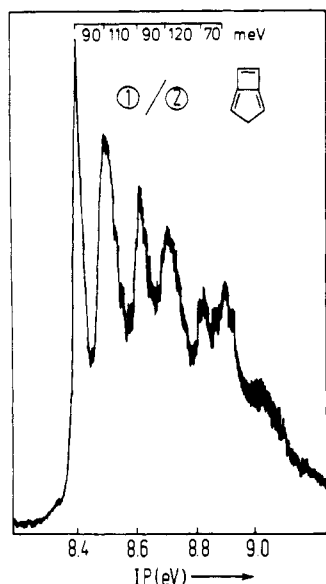


Figure 4. Section (covering bands 1 and 2) of the He I photoelectron spectrum of 2,5-dehydrotropylidene on an expanded scale. The numbers given on top of the spectral trace are the spacings between the resolved vibrational bands.

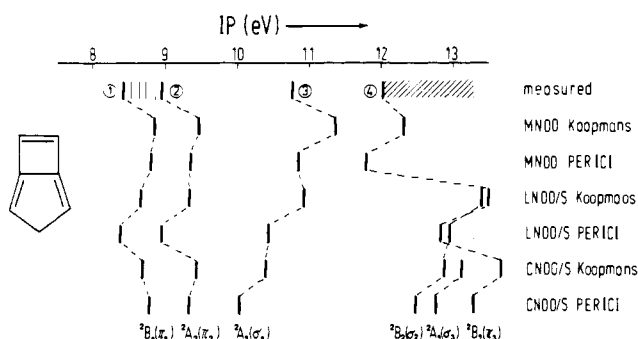


Figure 5. Measured and various calculated ionizations along with the respective ion state designations for bicyclo[3.2.0]hepta-1,4,6-triene (2,5-dehydrotropylidene).

it was necessary to collect a part of the respective fraction in a further trap containing deuteriochloroform or another suitable solvent. The solution of the triene could be transferred to an NMR tube without difficulties.

3-Oxabicyclo[3.2.0]hepta-1,4,6-triene. *trans*-1,2-Diethynyloxirane was pyrolyzed in a nitrogen flow system according to Vollhardt and Bergman.³ The pyrolysate was collected and transported into a trap which was cooled with liquid nitrogen and could be closed by stopcocks and connected to the inlet line of the PE spectrometer. The pyrolysate containing the extremely sensitive triene was directly introduced into the PE spectrometer. Appropriate pyrolysis conditions were determined by the following procedure. A solution of the oxirane in hexane was pyrolyzed and analyzed by GLC (Perkin-Elmer 900, 5% Carbowax 20M on Chromosorb W AW-DMCS, 1.8 m \times 1/8 in., 100 °C, 45 mL/min N₂). If some oxirane was detected the temperature of the oven was raised. This procedure was repeated until no oxirane was found by gas chromatography.

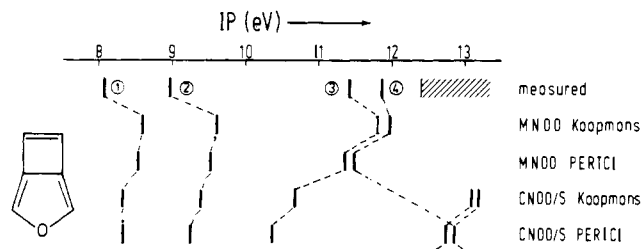


Figure 6. Measured and various calculated ionizations along with the respective ion state designations for 3-oxabicyclo[3.2.0]hepta-1,4,6-triene (3,6-dehydrooxepin).

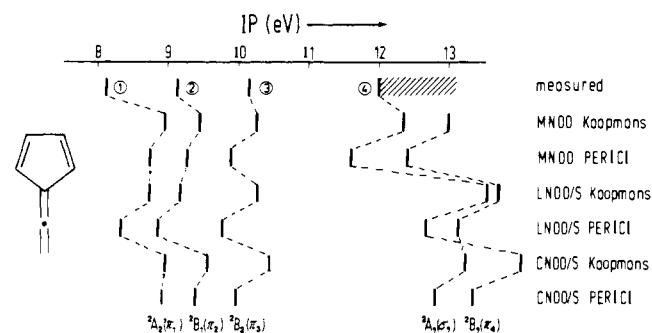


Figure 7. Measured and various calculated ionizations and respective ion state designations for fulvenallene.

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References and Notes

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