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An Analysis of the Electronic Structure of 6,7-Dimethyl-3-oxabicyclo[3.2.0]hepta-1,4,6-triene

*Reiner Sustmann**[a], *Wolfgang Müller*[a], *Wolfgang R. Roth*[b], and *Dieter Wittich*[b]

Institut für Organische Chemie der Universität Essen[a],
D-4300 Essen 1, Postfach 103764, and
Lehrstuhl für Organische Chemie 1, Ruhr-Universität Bochum[b],
D-4360 Bochum, Postfach 102148

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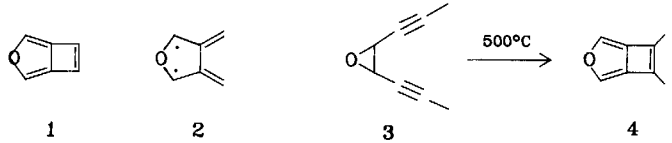
The geometry and the π-electronic structure of 6,7-dimethyl-3-oxabicyclo[3.2.0]hepta-1,4,6-triene (**4**) is analyzed by MNDO calculations and by the interpretation of the He-I-photoelectron spectrum. The calculated bond length alternations in **4** indicate olefinic resp. antiaromatic character. As HOMO and LUMO of **4** are mainly localized in the double bond of the cyclobutene subunit, electrophilic and nucleophilic reactions should occur at this bond. From the HOMO *IP* of 7.82 eV a high degree of nucleophilic character is to be expected.

Analyse der elektronischen Struktur von 6,7-Dimethyl-3-oxabicyclo[3.2.0]hepta-1,4,6-trien

Die Geometrie und π-Elektronenstruktur von 6,7-Dimethyl-3-oxabicyclo[3.2.0]hepta-1,4,6-trien (**4**) wurde mittels MNDO-Rechnungen und des He(I)-Photoelektronenspektrums analysiert. Auf Grund der Alternanz der Bindungslängen kommt dem Molekül olefinischer bzw. antiaromatischer Charakter zu. HOMO und LUMO sind im wesentlichen in der Doppelbindung des Vierrings lokalisiert. Die HOMO-Energie von 7.82 eV deutet auf einen hohen nucleophilen Charakter für **4**.

3-Oxabicyclo[3.2.0]hepta-1,4,6-triene (**1**), a cyclic 8 π-electron system, has been prepared some time ago and was shown to be stable only at low temperature[1]. In presence of oxygen it polymerizes instantaneously and with cyclopentadiene it undergoes [4 + 2]-cycloaddition at the double bond of the four-membered ring. In solution it dimerizes slowly to form a bisfurocyclooctatetraene *via* a [2 + 2]-cycloaddition and a ring opening reaction. In the course of studies on the 3,4-dimethylenefuran-2,5-diyl system **2** the 6,7-dimethyl analogue of **1**, namely **4**, has been prepared by thermolysis of **3**[2].



1 **2** **3** **4**

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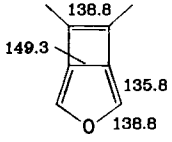
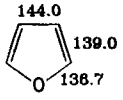
Here we report a photoelectron spectroscopical study in combination with MNDO calculations on **4**.

6,7-Dimethyl-3-oxabicyclo[3.2.0]hepta-1,4,6-triene (**4**) can be formed by union of furan and 1,2-dimethylcyclobutene, leading to the conjugated bicyclic 8 π-electron system. MNDO calculations with full geometry optimization[3] were therefore carried out for furan, 1,2-dimethylcyclobutene and **4**. The following structures (bond lengths in pm) and heat of formations were obtained.



4

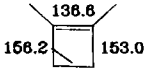
ΔH_f = 49.43 kcal/mol



5

ΔH_f = −8.68 kcal/mol

$\Delta H_{f(exp)}$ = −8.30 kcal/mol[4]



6

ΔH_f = 6.36 kcal/mol

The heterocyclic part of **4** shows higher double bond localization than furan, thus indicating a higher olefinic character of this part of the molecule. The common bond of the two rings is essentially a single bond even though shorter than in 1,2-dimethylcyclobutene. Both this and the 3,4-bond show similar lengths as those of single bonds between two sp^2-hybridized carbon atoms for instance in butadiene[5]. The double bond length of 138.8 pm demonstrates less localization of the π-bond than in 1,2-dimethylcyclobutene. From its structural data one can consider **4** as a cyclic conjugated 8 π-electron olefinic compound. Fig. 1 correlates the π-molecular orbitals of the two isolated molecules with those of **4**. Due to their symmetry and orbital energy one finds principal interaction between π_2 of furan and π of 1,2-dimethylcyclobutene leading to Φ_2 and Φ_4 of **4**. As π_3 of furan is only slightly lowered by its interaction with π* of **6** the orbitals Φ_3 and Φ_4 are reversed in order as compared to π_2 and π_3 of furan. The symmetric behaviour of the HOMO Φ_4 must have consequences for the reactivity of **4**. The second major orbital splitting concerns π_5 and π* leading to an antisymmetric nature of the LUMO of **4**.

Table 1. He-I-photoelectron spectroscopical vertical (v) ionization potentials for 6,7-dimethyl-3-oxabicyclo[3.2.0]hepta-1,4,6-triene (**4**)

1.	2.	3.	4.	5.	6.	7.	8.
7.62 7.75 7.82 (v)	8.80 8.88 (v)	11.20	12.00	12.42	13.50	14.23	16.40

The He-I-photoelectron spectrum of **4** (table 1 and fig. 2) can easily be interpreted in terms of the above analysis. The first three vertical ionization potentials occur at 7.82, 8.88 and 11.20 eV. Taking the first two experimental ionization

potentials of furan and for 1,2-dimethylcyclobutene an experimental value of 8.3 eV[6] one may construct the orbital diagram of Fig. 3.

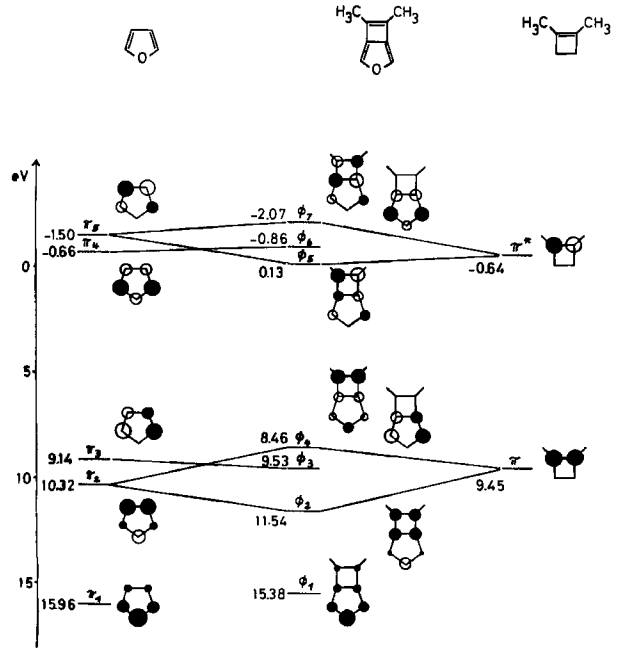


Fig. 1. Molecular orbitals and their relations for **4**, **5** and **6** according to MNDO calculations

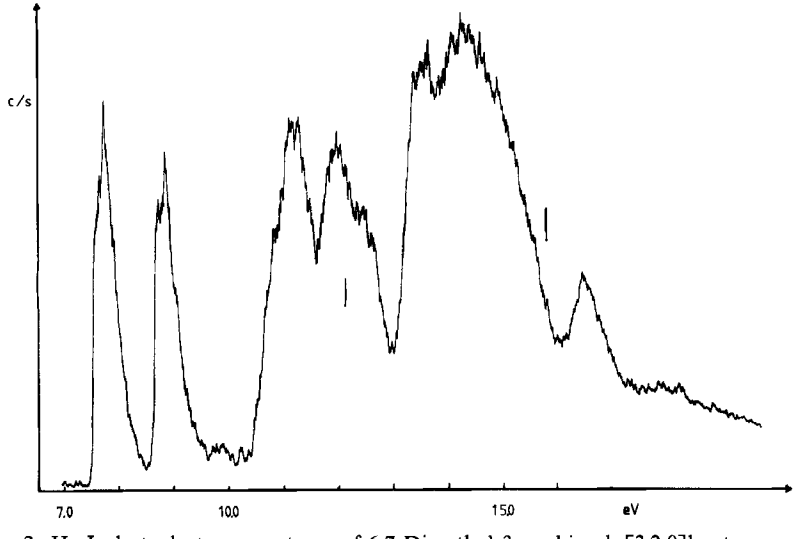


Fig. 2. He-I-photoelectron spectrum of 6,7-Dimethyl-3-oxabicyclo[3.2.0]hepta-1,4,6-triene (**4**)

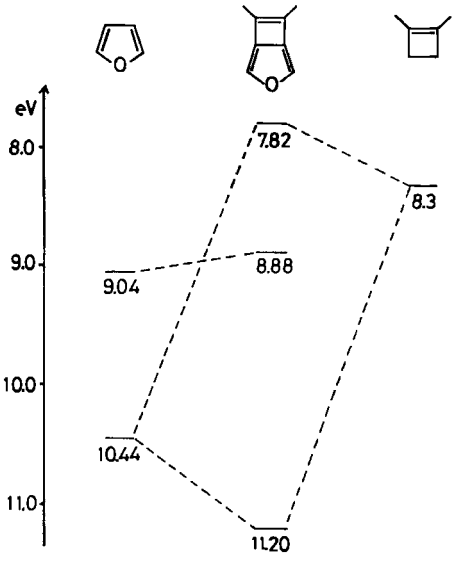


Fig. 3. Orbital interaction diagram for the π-MO's of **4**, **5** and **6** from experimental *IP*'s

In comparing furan with **4** one ionization potential (π_3) remains almost unaffected whereas the second one (π_2) is lowered in energy. As expected the highest *IP* is closest in energy to the HOMO of the olefin and the corresponding molecular orbital should be mainly localized in the double bond of the four-membered ring. According to the MNDO calculation the contribution of the double bond of the cyclobutene system in π_4 amounts to ca. 50%. The indicated vibrational progression of 970 cm^{-1} of the first band demonstrates that this *IP* is connected with the conjugated π-system.

The assignment of ionization potentials 4 through 8 to specific molecular orbitals does not seem to be very useful. According to the MNDO calculations they represent mainly molecular orbitals of σ-character. There must be one additional π-*IP* which by comparison with the calculation should be in the region of 15 to 16 eV.

As a result of the MNDO calculations and the interpretation of the photoelectron spectrum one anticipates that reagents whether electrophilic, attacking the HOMO, or nucleophilic, interacting with the LUMO, will react primarily at the double bond of the four-membered ring. [2 + 4]-Cycloadditions, if they are not influenced by steric hindrance, should occur at the tetrasubstituted double bond. Electrophilic additions of halogens also should be observed at this double bond. The experimental evidence[2] supports these conclusions.

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[6] This *IP* was estimated by subtracting 1.3 eV, the difference in π-*IP*'s between ethene and *cis*-2-butene, from the first ionization potential of cyclobutene (9.59 eV)[7].
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