Tetrahedron Letters, Vol. 34, No. 26, pp. 4245-4248, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Electronic Structure of Fused 7-oxanorbornenes. Photoelectronspectroscopic Study

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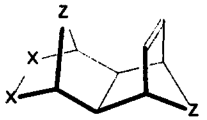
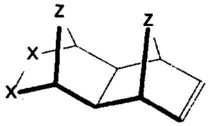
Abstract: PE analysis of 1 and 2 reveals considerable stronger interaction between both π- and n-levels in the latter compound.

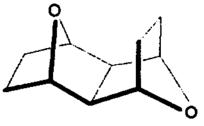
Fused 7-oxanorbornenes have gained considerable attention recently as potential bulding blocks of polarofacial spacers.[1] They are also quite challenging from spectroscopic point of view as they provide unique framework for studying interactions of proximate π- and/or n-orbitals.[2] In order to get deeper insight into intramolecular interactions among the valence orbitals of this class of compounds we measured the He (I) photoelectron (PE) spectra of bis-epoxides **1** and **2**.



1 X-X= CH=CH; Z=O
3 X-X= (CH(COOH))$_2$;Z=O
5 X-X= CH=CH; Z=CH$_2$



2 X-X= CH=CH; Z=O
4 X-X= (CH(COOH))$_2$; Z=O
6 X-X= CH=CH; Z=CH$_2$



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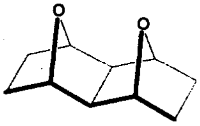

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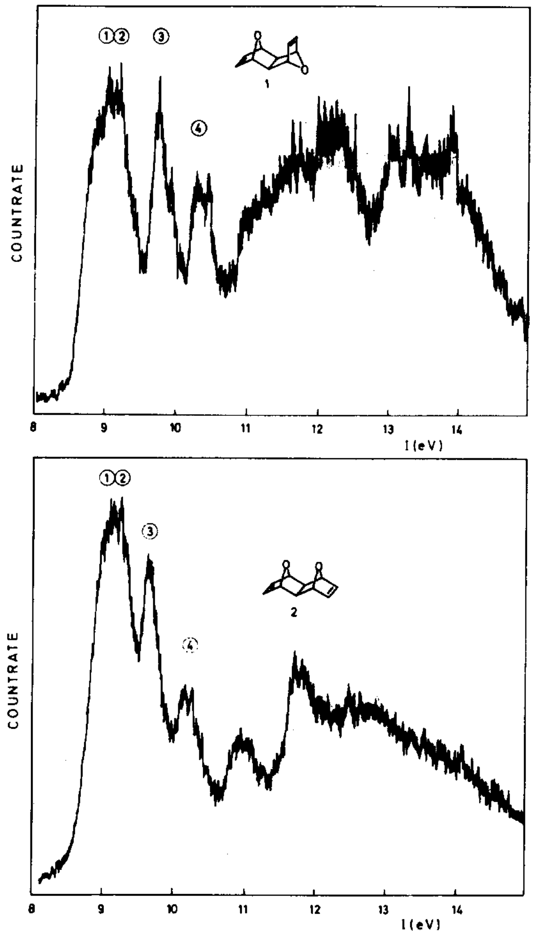

Figure 1. He(I) photoelectron spectra of **1** and **2**.

The spectra are analyzed by correlative analyses assisted by ab initio calculations emplo-ying STO-3G and 3-21G basis sets.[3]

Synthesis of the target epoxides **1** and **2** was achieved by electrolytic decarboxylation of the mixture of diacids **3** and **4**, followed by HPLC on porasil column (n-hexane: ethyl-acetate=1:4).[4]

The PE spectra of **1** and **2** (Figure 1) are found to be very similar in the low energy region.[6] Both of them exhibit three ionization features below 10.5 eV in the ratio 2:1:1. To assign their sequence in the PE spectrum of **1** we shall briefly consider the PE spectrum of compound **5**.[7]
The latter shows two bands at 8.46 and 8.90 eV well separated from the rest of the spectrum. They have been assigned to the ionization of the out-of-phase (π^-) and in-phase (π^+) linear combinations of the olephinic π-MO's. Concomitantly, we conclude that the first two bands (① and ②) in the PE spectrum of **1** are due to ionization from MO's of predominant π-character. Their shifts towards higher ionization energies (0.5 and 0.25 eV, resp.) relative to the corresponding values in **5** are anticipated as consequence of the inductive perturbation by the oxygen atoms,[8] hyperconjugative interaction between neighbouring π- and n-MO's[8] and change in the extent of through-bond coupling.[7,9]

Similarly, judging from the energy gap between the bands related to ionization from the out-of-phase (n^-) and in-phase (n^+) linear combinations of the 2p oxygen lone pairs in the *exo,endo*-epoxide **7**[2a] (0.54 eV) it seems reasonable to assign bands ③ and ④ to ionization of the MO's of dominant lone pair character. It should be noted that both bands are shifted by ~0.5 eV to higher energies relative to **7**. This is twice as large as observed on passing from 7-oxa-norbornane to 7-oxanorbornene.[8a] Finally, band assignments proposed above receive full support from the results of ab initio calculations (Table 1).

Table 1. Comparison between the First Vertical Ionization Energies ($I_{v,j}$) and the Calculated Orbital Energies, ϵ_j, According to ab initio Calculations Employing STO-3G and 3-21G Basis Sets for **1** and **2**[10]. All Values in eV.

Compound	Band	$I_{v,j}$	Asssign ment[11]	$-\epsilon_j$ STO-3G	$-\epsilon_j$ 3-21G
1 (C_s)	1	9.0	20a'(π^-)	7.79	9.21
	2	9.15	19a'(π^+)	8.25	9.67
	3	9.7	18a'(n^-)	9.05	11.13
	4	10.25	17a'(n^+)	9.62	11.79
2 (C_{2v})	1	9.0	$9b_1(\pi^-)$	7.86	9.31
	2	9.2	$8b_1(n^-)$	8.67	10.66
	3	9.58	$11a_1(\pi^+)$	8.59	10.14
	4	10.12	$10a_1(n^+)$	9.37	11.51

By similar reasoning, using **6**[12] and **8**[2a] as reference compounds, the first four ionization events in the PE spectrum of **2** are ascribed to ionizations from the following MO's: $\pi^- \approx n^- < \pi^+ < n^+$. The corresponding π-levels in the PE spectrum of **6**[12] are found at 8.48 and 9.35 eV, while the bands associated with ionizations from the lone-pair orbitals in the PE spectrum of **8**[2a] appear at 8.87 and 9.80 eV, respectively. It must be stressed, however, that both theoretical procedures place π^+ above n^-. On the other hand, qualitative arguments, such as spatial arrangement of the interacting semilocalized orbitals, according to which interaction between either π- (via through-bond mechanism) or n-levels (preferentially via through-space coupling) in **2** should be more efficient than in **1** suggest the opposite. We note in passing that this conjecture is supported by calculations, albeit only qualitatively (Table 1). For instance, 3-21G procedure predicts π,π-splitting energy of 0.46 eV for **1** compared to the value of 0.83 eV in **2**. The experimentally derived values are ~0.2 (in **1**) and ~0.5 eV (in **2**), respectively. The same theoretical method predicts an increase of the n,n-splitting on passing from **1** to **2** of 0.19 eV, whereas experimentally obtained value amounts to 0.37 eV.

Acknowledgement: This work has been supported by the Ministry of Science of Republic of Croatia. A part of the work was done at the Organisch-Chemisches Institut der Universität Heidelberg, and M.E.M. thanks Professor R. Gleiter for his kind hospitality and the Alexander von Humboldt Foundation for financial support. We are indebted to Mr. A. Flatow for measuring the PE spectra.

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4. All new compounds were characterized by the usual spectroscopic techniques and had satisfactory elemental analysis.[5]
5. Maksimović, Lj.; Novak, N. and Eckert-Maksić, M., submitted for publication.
6. The PE spectra were recorded with a PS18 spectrometer of Perkin Elmer, Ltd. (Beaconsfield, England) and were calibrated with Ar and Xe. A resolution of about 20 meV of the $^2P_{3/2}$ Ar line was obtained. The samples have to be heated to the following temperatures: **1**: 60^{0}C; **2**; 100^{0}C.
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10. The assumed correlation between ionization and orbital energies rests on the validity of Koopmans'theorem; Koopmans'.T. Physica **1934**, *1*, 104.
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(Received in UK 14 April 1993)