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Photoelectron Spectroscopy of Monocyclic Olefins.

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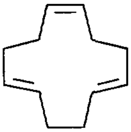
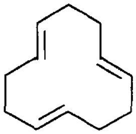
Abstract: We present He I photoelectron spectra (UPS) of several isomeric monocyclic trienes and dienes. The spectra were interpreted by semiempirical MO calculations and comparison with spectra of related compounds. The results suggest that in 1,5,9-cyclododecatriene the homoconjugative π,π-interactions are sensitive to E/Z molecular topology while in 1,9 -cyclohexadecadienes they are not. We have analyzed both π-ionization energies and σ-onset energies in order to unravel relative importance of through-space and through-bond interactions. We propose a new *trans rule* for monocyclic olefins. © 1997 Elsevier Science Ltd.

Introduction

Studies of large molecules which have several isolated functional groups are interesting because they can furnish details of possible intramolecular interactions. The method of choice for such studies is often VUV photoelectron spectroscopy (UPS). UPS can provide information not only about intramolecular interactions, but also about conformations of free molecules, even when standard physical methods (X-ray and electron diffraction, MW and NMR spectroscopy) can not do so[1]. C=C is one of the most common functional groups and numerous studies of interactions between nonconjugated π-bonds had been reported and summarized in the chemical literature[2,3]. The conceptual framework of through-bond (TB) and through-space (TS) interactions was used to rationalize pertinent experimental data. For studies of TB and TS, specially designed molecules were chosen , in which C=C groups were held in place by rigid σ-skeletons. The skeletons had various shapes e.g. chains, rings or cages[4]. Different relative positions of C=C groups require use of σ-skeletons of different shapes and sizes. However, C=C bonds can interact not only with each other, but also with σ-skeletons. If one uses a different σ-skeleton in order to fix C=C groups in certain relative positions, it may not always be easy to separate C=C/C=C from C=C/σ interactions. We shall describe the investigation of isomeric monocyclic trienes $C_{12}H_{18}$ (**1-3**) and dienes $C_{16}H_{28}$ (**4-6**).



1 (ZEE)



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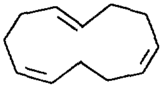

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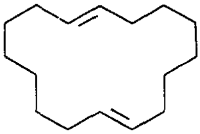

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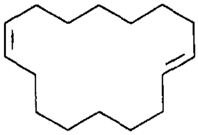

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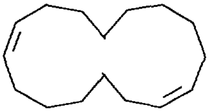


6 (ZZ)

The aim was to establish relative importance of TS and TB interactions as a function of E/Z isomerism and also to obtain some conformational information about **1-6**. This is important in view of the fact that very few studies had been reported concerning conformation and electronic structure of large monocyclic olefins with *cis* and *trans* double bonds.

Experimental

The sample compounds were obtained from the commercial source (Fluka AG) and their purity (>97%) was checked by GC. UPS spectra were recorded on a modified Perkin-Elmer PS16/18 spectrometer. Spectra were calibrated by adding small amounts of N_2O to the sample flow and by reference to the $1b^{-1}$ H_2O peak originating from traces of water present in the sample. Spectra were recorded with a resolution of 20 meV (FWHM) as measured for the Ar $^2P_{3/2}$ HeI spectrum. AM1 calculations were performed with Spartan 4.1 software package[5] and included full geometry optimization.

Results and Discussion

He I photoelectron spectra of 1,5,9-cyclododecatrienes **1-3** are shown in Figure 1.

The spectra of 1,9-cyclohexadecadienes **4-6** are not shown, because all of them have very similar appearance and consist of a single band with maximum at 8.87 ± 0.1 eV followed by the σ-onset at 9.9 eV. Two regions can be distinguished in the spectra of **1-6**. The region below 10 eV consists of bands corresponding only to π-orbital ionizations, while the region above 10 eV contains bands originating from ionization of σ-orbitals only. This assignment is supported by the AM1 calculations and comparison with the spectra of other cyclic olefins[6-8]

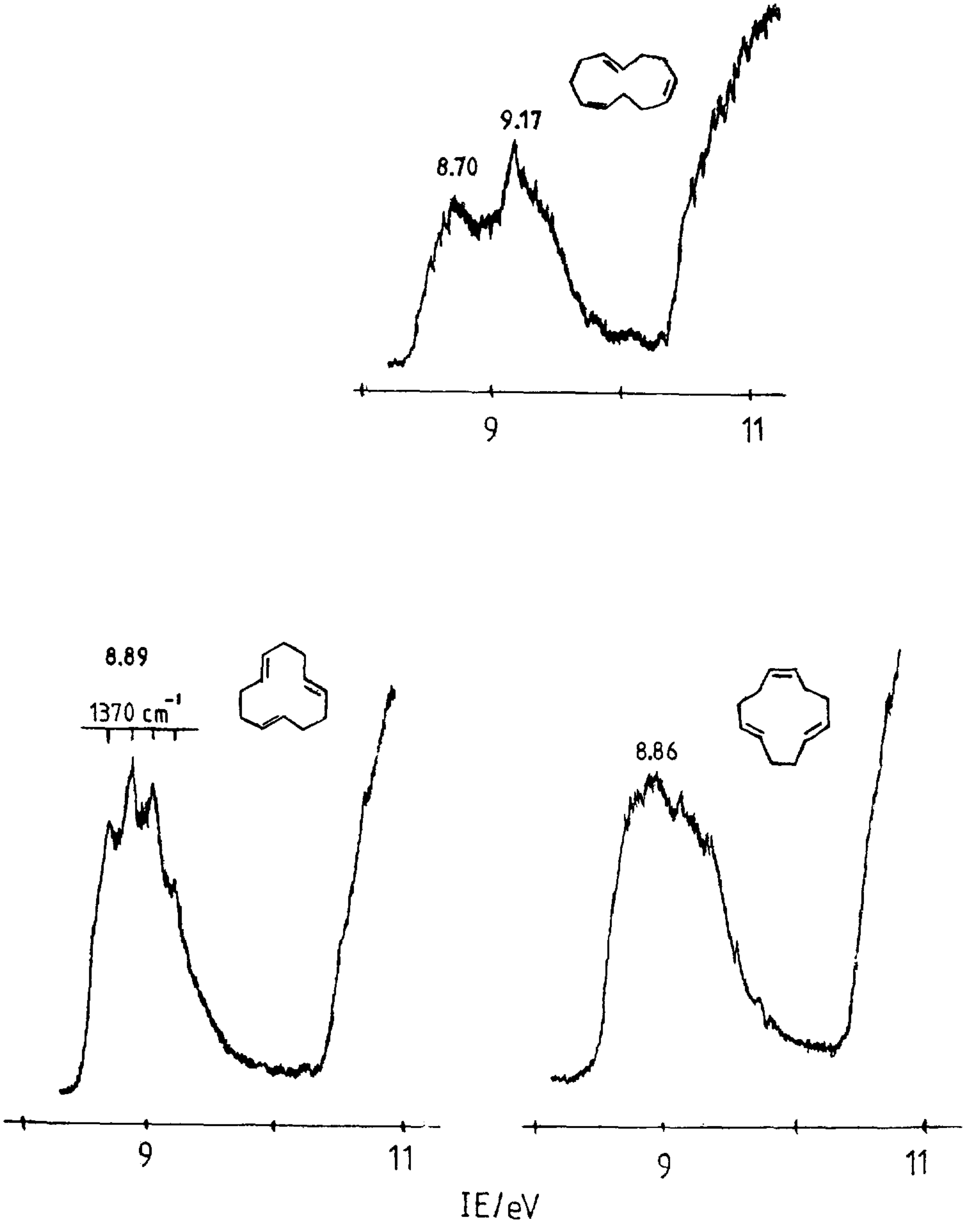
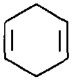


Figure 1: He I photoelectron spectra of isomeric 1,5,9-cyclododecatrienes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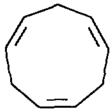
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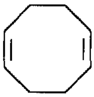
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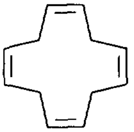
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Several π-bands in **1-6** exhibit vibrational progressions of 1370 cm^{-1} which correspond to C=C stretching modes. This vibrational fine structure further supports the given assignments. The analysis of the spectra provides information regarding the nature of π-orbital interactions in **1-6**. In the studies reported previously, the conclusions about TS or TB interactions were reached mainly on the basis of the energy difference (splitting) between π-bands . However, we have considered in addition to π-band splitting, the energies of the σ-onset and of the absolute values of π-band ionization energies. This should provide information about the relative significance of TB and TS interactions.

The average values of π-ionization energies in **1-6** are similar, which suggests that TB interactions are not significant. If they were significant, one would expect to observe different π-ionization energies for dienes and trienes which have different σ-skeletons. The difference in σ-skeletons is reflected in σ-onsets which are at 9.9 and 10.4 eV for dienes and trienes, respectively. As can be expected, σ-onsets in dienes appear at lower energy than in trienes, because there are more σ-orbitals in C_{16} than in C_{12} alkenes.

Spectra of **1-3** show interesting variations in the widths of π-bands (Fig.1). ZZE isomer has a prominently split π-band (0.57 eV). EEE isomer has narrow π-band with no observable splitting, while ZEE isomer has broad band with unresolved shoulder. These variations can be rationalized by different degrees of TS interactions in the three molecules. TB interactions are of the same magnitude as is suggested by identical σ-onsets. The extent of TS interactions decreases along the series: ZZE > ZEE > EEE. This empirical conclusion is important in the view of the fact that AM1 calculations (interpreted via Koopmans approximation) are not able to reproduce clearly trends in MO energies. The calculations suggest that variations in π-orbital energies along the isomers sequence are of the order of 0.1 eV.

It may be suggested that the presence of various conformers can also influence observed bandwidths. This is unlikely in view of the NMR studies[9,10] which have indicated the presence of a single conformer (for each triene) at ambient temperatures. The interconversion barriers for different conformers are fairly high (> 25 $kJmol^{-1}$). Our results are in agreement with NMR data which have indicated that symmetries of the triene isomers are D_3 (EEE), C_{2v} (ZEE) and C_s (ZZE). As can be expected, the molecule with the highest symmetry D_3 has degenerate occupied MOs (a_1+e symmetry) and the smallest bandwidth.

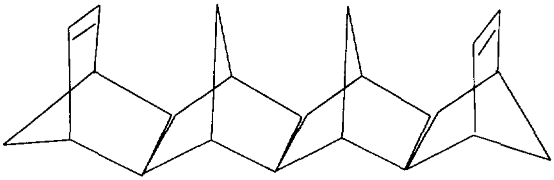
1,4-π,π-interactions in **1-3** are very sensitive to molecular topology. This sensitivity had also been noticed in 1,4-cyclooctadienes (**9**) which, like **1-3** contain nonconjugated C=C bonds separated by two methylene spacer groups. The spectrum of EZ isomer[11] shows π-band splitting of 0.3 eV while ZZ isomer[6] has no resolvable splitting. On the basis of the limited set of UPS data reported previously[7,11,12] and in this work we can propose a new *"trans rule"* which states that the larger the number of trans C=C bonds present in a monocyclic olefin, the larger the homoconjugation. (The rule is applicable to 1,4-π,π- and 1,5-π,π-interactions). The validity of the rule could be tested from its predictions of as yet unknown spectra:

a) EE isomer should show the largest π-band splitting amongst 1,4-cyclooctadienes

b) ZZZ isomer of 1,5,9-cyclododecatriene should have no splitting

The attempts at verification of the rule should stimulate further research e.g. by trying to establish whether the rule applies to 1,3-π,π-interactions. A UPS studies of all-E isomers of 1,4,7-cyclononatriene and 1,4,7,10-cyclododecatetraene might be useful in this respect.

Finally, a comparison between dienes **4-6** and **11** is interesting because these molecules have nominal 1,9-π,π-interactions. However, the spectra of **4-6** show no π-band splitting while **11** has the splitting of 0.29 eV[3]. The splitting was attributed to laticyclic hyperconjugation which is present in **11**, but absent in **4-6**.



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Conclusion

The 1,9-π,π-interactions in monocyclic dienes are insignificant and hence independent of molecular topology (E/Z isomerism). 1,4-π,π-interactions in monocyclic trienes are significant and strongly influenced by molecular topology (E/Z isomerism) with TS interactions being more prominent than TB.

We have demonstrated how a clear distinction between TS and TB interactions can be made from the UPS results. One needs to consider in addition to the usual analysis of π-band splitting, the absolute values of ionization energies for π-bands and σ-onsets.

ACKNOWLEDGMENTS:

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REFERENCES:

1. Novak, I.; Potts, A.W. *J.Org.Chem.* **1996**, *61*, 786.
2. Gleiter, R.; Schäfer, W. *Acc.Chem.Res.* **1990,** *23*, 369.
3. Paddon-Row, M.N.; Jordan, K.D. In *Modern Models of Bonding and Delocalization*; Liebman, J.F., Greenberg, A. Eds., Verlag-Chemie: Weinheim, 1988; p.115.

4. Borzyk, O.; Herb, T.; Sigwart, C.; Gleiter, R. *Pure Appl.Chem.* **1996**, *68*, 233.
5. Spartan ver. 4.1, Wavefunction Inc., Irvine, CA 92715
6. Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J.P. *Helv.Chim.Acta* **1977**, *60*, 2213.
7. Bischof, P.; Gleiter, R.; Heilbronner, E. *Helv.Chim.Acta* **1970**, *53*, 1425.
8. Krause, A.; Musso, H.; Boland, W.; Ahlrichs, R.; Gleiter, R.; Boese, R.; Bär, M. *Angew.Chem.Int.Ed.Engl.* **1989**, *28*, 1379.
9. Radeglia, R.; Poleschner, H.; Haufe, G. *Magn.Reson.Chem.* **1993**, *31*, 1054.
10. Rawdah, T.N.; El-Faer, M.Z. *Tetrahedron Lett.* **1995**, *36*, 3381.
11. Martin, H.-D.; Kunze, M.; Beckhaus, H.-D.; Walsh, R.; Gleiter, R. *Tetrahedron Lett.* **1979**, 3069.
12. Bischof, P.; Heilbronner, E. *Helv.Chim.Acta* **1970**, *53*, 1677.

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