Photoelectron Spectroscopy of Heterocycles. Phenyloxiranes

H. Güsten *, L. Klasinc, I. Novak, and M. Šanjek
The Rudjer Bošković Institute, Zagreb, Croatia, Yugoslavia

Z. Naturforsch. **39 a**, 1230 – 1234 (1984); received November 10, 1984

Dedicated to Professor D. Schulte-Frohlinde on the occasion of his 60th birthday

The HeI photoelectron spectra of 2-phenyloxirane, 2,2-diphenyloxirane, trans-2,3-diphenyloxirane, 2,2,3-triphenyloxirane, and 2,2,3,3-tetraphenyloxirane are reported. Comparison with the spectra of ethylene oxide (oxirane), benzene, and the following phenylethenes–styrene (1), 1,1-diphenylethene (2), cis-stilbene (3), trans-stilbene (4), triphenylethene (5), and tetraphenylethene (6) – allowed to assign the lower ionization energies of the phenyloxiranes. Splitting of the lowest energy benzene π-orbitals is qualitatively the same in both classes of compounds. Because of the perpendicular orientation of the oxygen lone-pair in comparison to the π-electrons of the ethylene double bond this splitting is considerably smaller in phenyloxiranes.

Introduction

The interesting electronic structure and properties of saturated three-membered rings have been extensively studied in the last thirty years. In order to describe bonding in these compounds concepts such as bent bonds [1, 2], ring strain, internal and external σ-orbitals (Walsh orbitals) [3], and through-space interaction [4] were introduced. Molecular photoelectron (PE) spectroscopy as a method yielding direct information about the electronic structure (Koopman's theorem) proved to be an important support in these studies. Thus, the ionization energies of ethylene oxide (oxirane) measured by PE spectroscopy were reported by Al Joboury and Turner [5] as early as in 1964, and several groups reported its PE spectrum and discussed its electronic structure in the following years [6 – 9]. Presently, we can take as confirmed the electronic structure of oxirane – at least as far as the two lowest energy levels (highest occupied orbitals) are

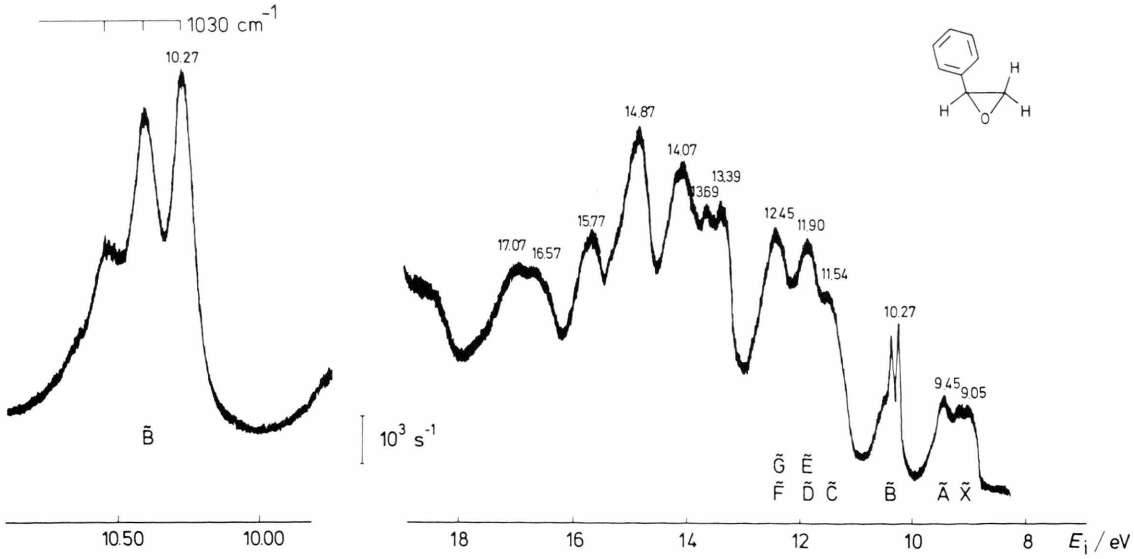

Fig. 1. He I photoelectron spectrum of 2-phenyloxirane with the $\tilde{B}$ system in high resolution.

Reprint requests to Dr. Hans Güsten, Kernforschungszentrum Karlsruhe, Institut für Radiochemie, Postfach 36 40, D-7500 Karlsruhe.

* Kernforschungszentrum Karlsruhe, Institut für Radiochemie, Federal Republic of Germany.

0340-4811 / 84 / 1200-1230 $ 01.30/0. – Please order a reprint rather than making your own copy.

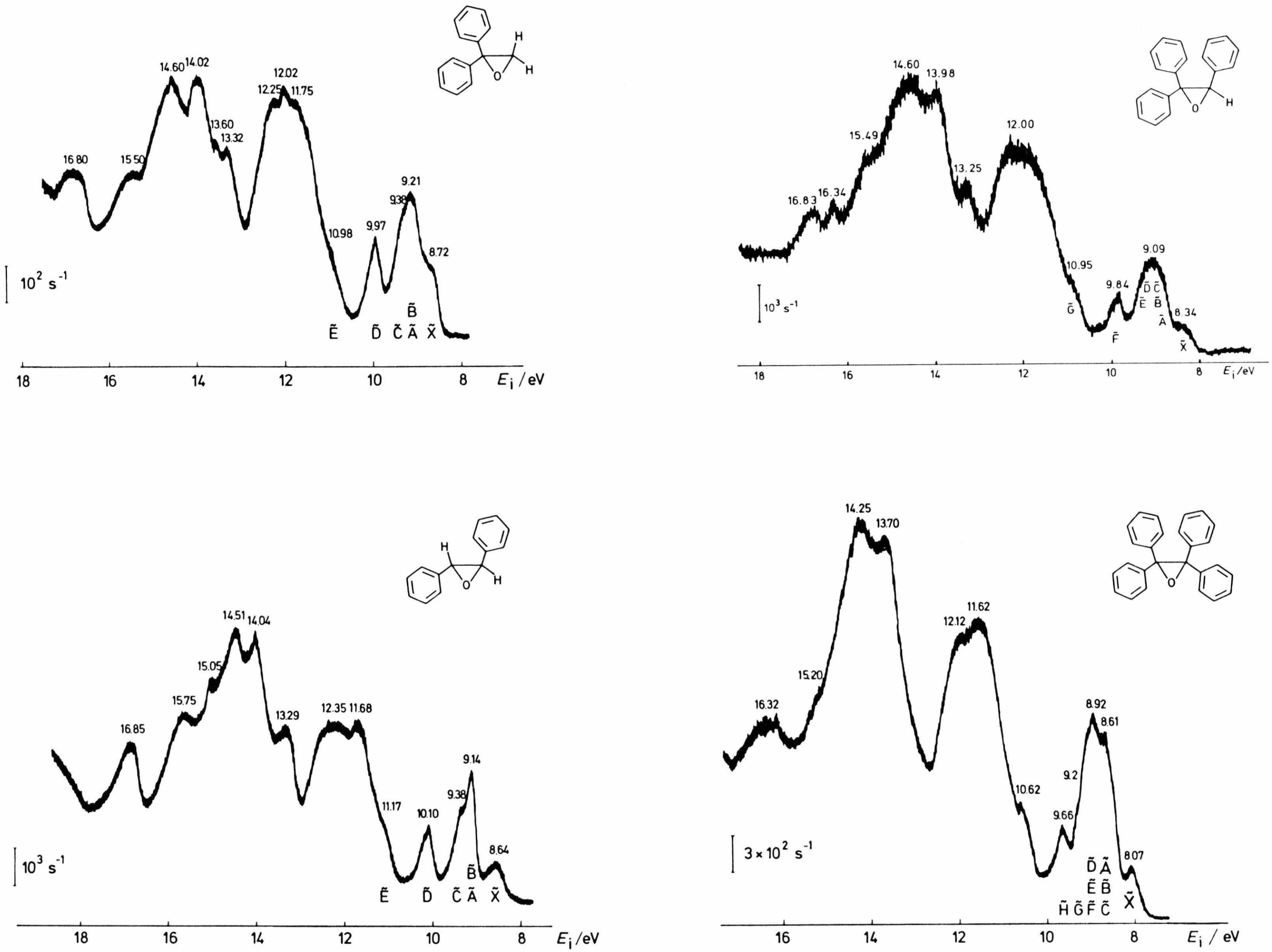

Fig. 2. He I photoelectron spectra of a) 2,2-diphenyloxirane, b) trans-2,3-diphenyloxirane, c) triphenyloxirane and d) tetraphenyloxirane.

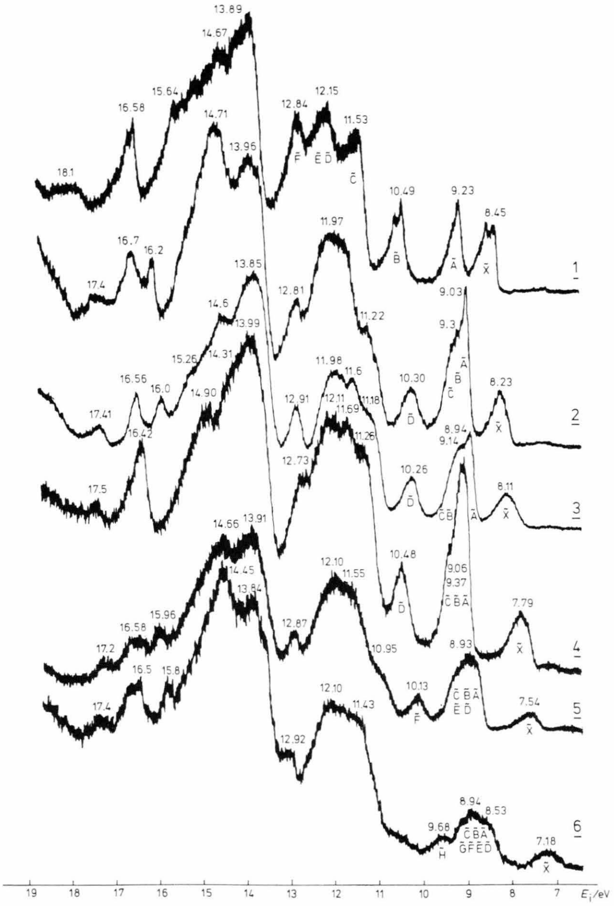

Fig. 3. He I photoelectron spectra of phenyl substituted ethenes: styrene (1), 1,1-diphenylethene (2), cis-stilbene (3), trans-stilbene (4), triphenylethene (5) and tetraphenylethene (6).

concerned. With this in mind we investigated the effect of phenyl groups on these levels and the effect of the oxirane ring on the π-levels of benzene. With geminal two, three or four phenyl groups the phenyloxiranes can become overcrowded which could possibly be observed in their PE spectra. Among the phenyloxiranes only the PE spectrum of 2-phenyloxirane has so far been reported [10]. However, much PE work has been done on the phenylethenes, styrenes and stilbenes [11–13], especially on their correlation with ethylene and benzene. The assignment of lower ionizations in these compounds can be taken as confirmed. Therefore for comparison with the PE spectra of the phenyloxiranes, in this work the PE spectra of the phenyl substituted ethenes were also investigated.

Experimental

The HeI spectra of oxirane, 2-phenyloxirane (I), 2,2-diphenyloxirane (II), trans-2,3-diphenyloxirane (III), 2,2,3-triphenyloxirane (IV) and tetraphenyloxirane (V) and the following phenylethenes – styrene (1), 1,1-diphenylethene (2), cis-stilbene (3), trans-stilbene (4), triphenylethene (5), and tetraphenylethene (6) – have been recorded on a Vacuum Generators UVG3 photoelectron spectrometer. The samples II to V were of commercial origin (EMKA-Chemie). Elevated temperatures of the inlet system for II, IV, V, VI, and **2–6** of 70 °C, 85 °C, 130 °C, 170 °C and 60 °C, 50 °C, 100 °C, 120 °C, 200 °C were employed to produce satisfactory spectra. The energy scale of the PE spectra was calibrated by simultaneous addition to the samples of small amounts of argon, xenon and nitrogen. The accuracy of the ionization energies quoted is ± 0.05 eV.

Results and Discussion

The low resolution HeI PE spectrum of 2-phenyloxirane (Fig. 1) and of II, III, IV, and V (Fig. 2a–d) and of the phenylethenes **1–6** (Fig. 3) are shown with the numbers on the top corresponding to the vertical ionization energies, $E_{i,v}$/eV and the standard notation of the observed electronic band systems indicated below. A correlation diagram of the lowest ionization energies of benzene and ethylene with those of the phenylethenes as well as of benzene and oxirane with those of the measured phenyloxiranes is shown in Figure 4. It can be seen that in all PE spectra, like in the PE spectrum of oxirane [6–9], there is a gap after 10 eV and again at about 13 eV. Moreover, these band systems are the two assigned lowest ionization energy systems of oxirane which only appear in the lower part of the spectrum: the $\tilde{X}$ system corresponding to a π ($2b_2$)-ionization at 10.55 eV and the $\tilde{A}$ system corresponding to a Walsh type σ ($6a_1$)-ionization at 11.86 eV. The former, in agreement with its mainly oxygen lone-pair character, has a very intensive O–O band and progressions in 1130 cm^{-1} and 630 cm^{-1} with rapidly falling intensities. In the second, if the onset at 11.10 eV is taken as the O–O band, the maximum of the rather diffuse system is reached at ν_3 with a wavenumber of about 1600 cm^{-1}.

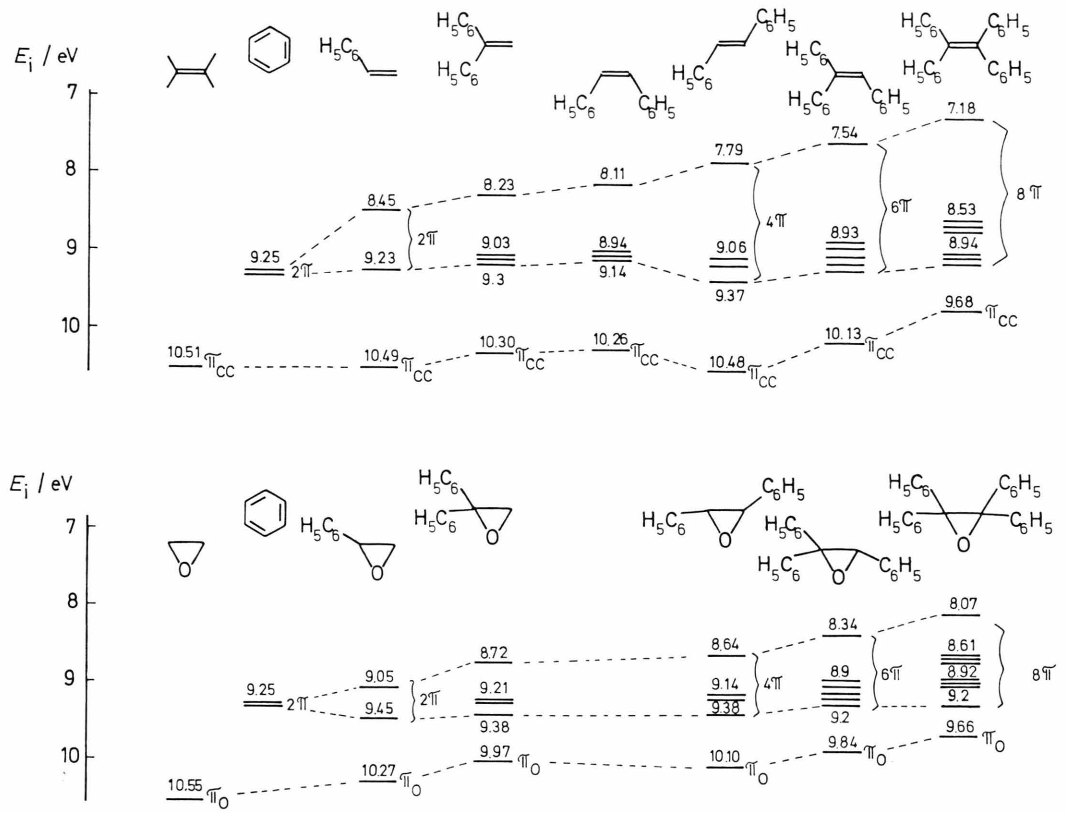

Fig. 4. Orbital correlation diagramme for benzene, ethylene, oxirane and the phenyl substituted ethenes (1–6) and phenyl substituted oxiranes (I–V).

What happens to these energy levels when a phenyl group is attached to oxirane can be observed in the PE spectrum of I (Fig. 1) and is indicated also in the correlation diagram in Figure 4. In agreement with the assignment of Akiyama et al. [10], systems at 9.05 eV and 9.45 eV are assigned to benzene π-ionizations. The structured $\tilde{B}$ system at 10.27 eV with a progression of $\nu = 1030\ \mathrm{cm}^{-1}$ is assigned to the oxygen lone-pair π_0 ionization (see Figure 1). Thus, considering the ionization energies the π-ionization of the ethylene double bond is replaced by an ionization of a lone-pair electron located mainly at the oxygen. However, the orientation of this lone-pair is perpendicular in comparison to that of the original ethylene π-electrons. It is therefore expected that in the PE spectra of phenylethenes **1–6**, in comparison to those of the phenyloxiranes I–V, a stronger splitting of the benzene π-levels will be observed. This is completely confirmed by the correlation shown in Figure 4. It also indicates that in the PE spectra of phenyloxiranes, contrary to expectations in this study, geminal phenyl groups do not cause significant effects of overcrowding.

Acknowledgements

This work was performed within a German-Yugoslav scientific cooperation programme. The financial support by Internationales Büro, Kernforschungsanlage Jülich and by the Republic Council for Science (SIZ II) of Croatia is gratefully acknowledged. We thank Professor G. Märkl of the University of Regensburg for a pure sample of 2-phenyloxirane.

[1] C. A. Coulson and W. E. Moffit, Phil. Mag. **40,** 1 (1949).
[2] R. Bonaccorsi, E. Scrocco, and J. Tomasi, J. Chem. Phys. **52,** 5270 (1970).
[3] A. D. Walsh, Nature London **159,** 165 (1947).
[4] R. Hoffmann, Acc. Chem. Res. **4,** 1 (1971).
[5] N. I. Al Joboury and D. W. Turner, J. Chem. Soc. **1964,** 4434.
[6] H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, J. Chem. Phys. **51,** 52 (1969).
[7] A. Schweig and W. Thiel, Chem. Phys. Lett. **16,** 541 (1973).
[8] D. H. Aue, H. M. Webb, W. R. Davidson, M. Vidal, M. T. Bowers, H. Goldwhite, L. E. Vertal, J. E. Douglas, P. A. Kollman, and G. L. Kenyon, J. Amer. Chem. Soc. **102,** 5151 (1980).
[9] E. J. McAlduff and K. N. Houk, Can. J. Chem. **55,** 318 (1977).
[10] I. Akiyama, K. C. Li, P. R. LeBreton, P. P. Fu, and R. G. Harvey, J. Phys. Chem. **83,** 2997 (1979).
[11] J. P. Maier and D. W. Turner, J. Chem. Soc. Faraday Trans. II, **69,** 169 (1973).
[12] L. Klasinc, Pure Appl. Chem. **52,** 1509 (1980).
[13] E. Hasselbach, U. Klemm, R. Gschwind, T. Bally, L. Chassot, and S. Nitsche, Helv. Chim. Acta **65,** 2464 (1982).