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CYCLIC PEROXIDES: DIHEDRAL ANGLE AROUND THE PEROXIDE BOND BY MICROWAVE AND PHOTOELECTRON SPECTROSCOPIC STUDIES

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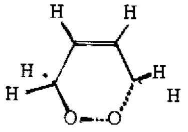
Abstract· Experimental COOC dihedral angles are used to support the relation proposed by Coughlin et al. for correlating the observed photoelectron splitting $n(O)^{\pm}$ with the dihedral angle around the peroxide bond in cyclic peroxides.

Cyclic peroxides represent an important class of compounds, often used as valuable synthetic intermediates, but little information is available on the structure of this kind of molecules.[1] Photoelectron investigations were recently carried out on some peroxides to reveal a dependence of the separation of the two highest orbitals (designated as an antisymmetric and a symmetric combination of the oxygen lone pairs, n^+ and n^-),[2] upon the dihedral angle around the peroxide bond.[3-5] Calculation for acyclic peroxides showed that the splitting of the two highest MO's should have maximum values at $\theta=0°$ and 180° and become degenerate at $\theta=90°$, where the two orbitals cross each other.[4-6] On the other hand, Coughlin, Brown, and Salomon[7] found a straight-line relation between the observed splittings and the dihedral angles estimated from Dreiding models for a series of peroxide compounds.[8]

Accidentally we have been studying the molecular structure of cyclic peroxides, 3,6-dihydro-1,2-dioxin (1) and 1,2-dioxolane (2), by microwave spectroscopy. This letter presents our results in support of the relation proposed by Coughlin et al.[7], with authentic values of angles determined by the experiment.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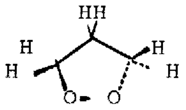
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The dihydrodioxin 1 was prepared by a photosensitized oxygenation of 1,3-butadiene,[9] while the dioxolane 2 was obtained from alkyl trifluoromethanesulfonate (triflate) and tri-n-butyltin peroxide in methylene chloride.[7] The microwave spectra of both compounds were observed at -40°C with a conventional

110 kHz modulated spectrometer. The rotational constants of the dioxolane were determined to be A=7500.0, B=7328.4, and C=4209.8 MHz, and those of the dioxin to be A=5287.43, B=5110.21, and C=2857.85 MHz.[10] The observed rotational constants of the dioxolane 2 were fairly well reproduced by the plausible set of the bond lengths, r_{C-C}(1.536 Å), r_{C-O}(1.428 Å), and r_{C-H}(1.10 Å), and the bond angles borrowed from analogous molecules. The bond angles in the skeletal framework were then allowed to adjust themselves slightly and resulted in ∠CCO =105.1° and ∠CCC=101.7°. Similar treatment was also carried out for the dioxin 1.[10] The dihedral angles for the dioxin 1 and the dioxolane 2 were obtained to be 80±2° and 50±2°, respectively. These dihedral angles were rather insensitive to the small variations in the structural parameters of the framework The details of the microwave spectroscopic study shall be reported elsewhere.

The photoelectron spectrum of the dioxolane 2 was already reported by Coughlin et al.[7], the splitting being determined to be 1.27 eV. We measured the He I photoelectron spectrum of the dioxin 1, using a JASCO photoelectron spectrometer. Figure 1 shows the observed spectrum. The first band has a vibrational structure to be assigned to the ionization of π(C=C) electrons: I_a=9.66 eV, slightly lower than that of ethylene (I_a=10.51 eV).[11] In the region of 10-11 eV, we observed a single peak with a maximum at 10.37 eV and with no evidence of splitting nor of a shoulder, in contrast to our expectation of two peaks which originate from the ionization of two kinds of lone-pair electrons of oxygen atoms $n(O)^+$ and $n(O)^-$. Our recent ab initio calculation[12] showed that (1) the highest occupied MO is the π(C=C), (2) the second and third inner MO's are mainly due to $n(O)^-$ and $n(O)^+$, respectively, and (3) the orbital separation between $n(O)^-$ and $n(O)^+$ is 0.23 eV. Therefore, we conclude that the two peaks to be expected in this region would merge into one and the splitting, if exists, does not exceed 0.4 eV, the separation between the 10.37 eV peak and the first vertical ionization potential (9.92 eV).

The above results for the two compounds are inserted onto Figure 4 of the paper by Coughlin et al.[7] and the resulting figure is given as Figure 2. The dihedral angle of 1,2-dioxolane 2 estimated on the Dreiding model was found to be smaller by about 20° than the actual value. The microwave structural determination of 3,3,5,5-tetramethyl-1,2-dioxolane, which is the compound corresponding to the point directly below 1,2-dioxolane 2, is hard to carry out because of the existence of four methyl internal rotor. The actual dihedral angle of this compound should also be moved to a value near 50°, since this is the same ring system as the dioxolane 2. The X-ray diffraction study of 1,4-diphenyl-2,3-dioxabicyclo[2.2 1]heptane[13] showed that its dihedral angle is 0°. The new curve shown in Figure 2 is supported by three authentic values of the dihedral angle at both ends and in the middle ($\theta\approx 0$, 50, and 80°). In contrast the old curve by Coughlin et al.[7] was drawn using the dihedral angles based on the Dreiding model. The deviation from the straight line can be guaranteed by the theoretical consideration referred above[4-6]: the energies of the two nonbonding orbitals do not depend linearly on the dihedral angle around the peroxide bond, rather with a slight curvature stated above.

We have shown in the above that the relation suggested by Coughlin et al.[7] is supported by the dihedral angles determined by microwave spectroscopy, with a slight improvement in their curve, and the relation can be safely used to predict the dihedral angle around the peroxide bond for this kind of molecules. The photoelectron spectroscopy can thus work as a valuable tool for deriving the conformation of cyclic peroxide molecules for which the structure determination is hard to carry out.

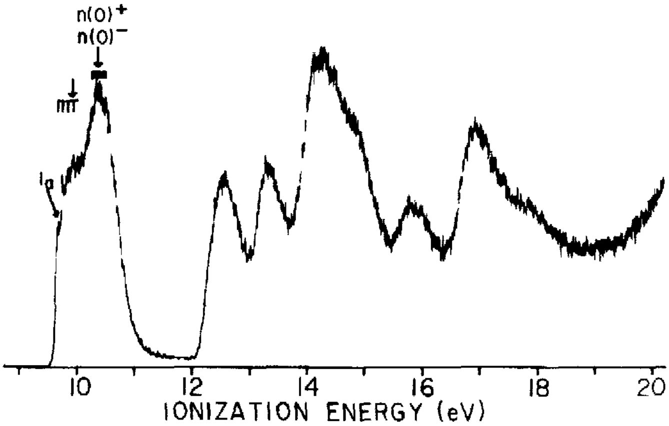

Figure 1. He I photoelectron spectrum of 3,6-dihydro-1,2-dioxin 1

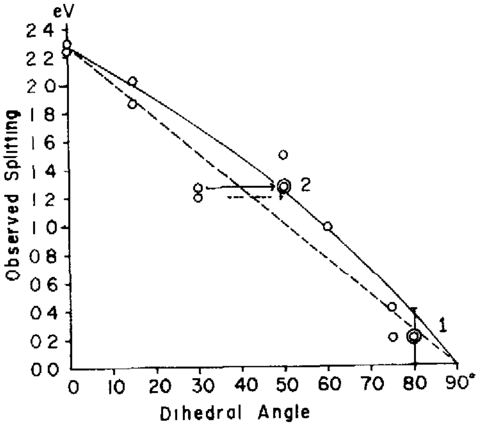

Figure 2. Observed splitting vs. dihedral angles for cyclic peroxides. Open circles and the broken line represent data taken from Coughlin et al.[7] Double circles are the present results and are using the dihedral angles determined experimentally.

Acknowledgement The authors are grateful to Professor Yonezo Morino for many helpful discussions.

References and Notes

1) D. Swern, Ed., "Organic Peroxides", Wiley-Interscience, New York, N. Y., 1970.

2) Brown[3] assigned the two highest MO's in the peroxide molecules to the antisymmetric combination of the oxygen lone pairs (n_O^-) and the antisymmetric combination of the C-O σbonds (σ^-). We preferred the assignment used in the text.

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8) Coughlin et al. mentioned that the values of the dihedral angles used for the discussion were only approximate, since torsional effects and vicinal O-O interaction were ignored in the Dreiding model.[7]

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12) The details of the ab initio calculation will be published elsewhere.

13) D. A. Langs, G. T. DeTitta, D. J Coughlin, and R. G. Salomon, result cited in Ref. 7).

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