Tetrahedron Letters No. 29, pp 2791 - 2794, 1973. Pergamon Press. Printed in Great Britain.

# THE PHOTOELECTRON SPECTRUM OF OXETANE: NON-DEGENERATE WALSH ORBITALS IN A FOUR-MEMBERED HETEROCYCLE

Phillip D. Mollere

(Department of Chemistry, Cornell University, Ithaca, N.Y.)

**(Received in USA 9 April 1973; received in UK for publication 11 June 1973)**

The properties of small ring compounds have long been a topic of interest; particular attention has been focused on the electronic structure of these highly strained molecules, and on the conjugative ability of their high-lying Walsh $\sigma$-orbitals. Of special note have been two relatively recent publications dealing with cyclobutane: one, in which the assigned photoelectron spectrum was reported [1], and a second paper, in which the valence orbitals (especially the degenerate pair of Walsh $\sigma$-orbitals) are discussed in terms of molecular orbital theory [2].

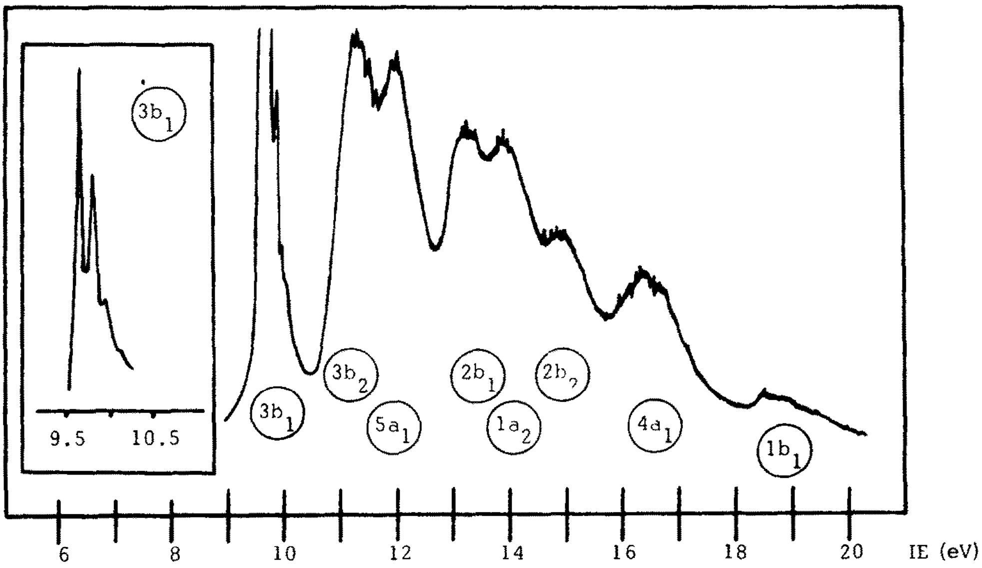
Oxetane (trimethylene oxide) is isoelectronic with cyclobutane. Its electronic structure, however, differs from the carbocyclic compound in at least two respects, as revealed by photoelectron spectroscopy (source energy = 21.21 eV) and molecular orbital calculations (CNDO/2 and EHT). (All calculations were carried out using the known planar ($C_{2v}$) structure of oxetane [3] and a planar ($D_{4h}$) model of cyclobutane. Although the equilibrium geometry of the latter is puckered [4], Hoffmann [2] found that the degeneracies and orbital shapes of $D_{2d}$ cyclobutane were retained in the $D_{4h}$ form; CNDO/2 calculations also show retention of these features, as well as only small changes in eigenvalues, upon flattening of the ring.)

The assigned photoelectron spectrum of oxetane is presented in Figure 1.

The first band is assigned to the $3b_1$ orbital, corresponding to the $\pi$-type "lone pair" on oxygen. The band shape (a very strong adiabatic transition, followed by rapidly diminishing $0\rightarrow1$, $0\rightarrow2$, and $0\rightarrow3$ transitions) is characteristic of nonbonding electron pairs, and the ionization energy ($IE_1$ = 9.63 eV) agrees very well with that determined from a Rydberg series (IE = 9.67 eV) [5]. Moreover, the vibrational fine structure arising from hyperconjugation of the "lone pair" with neighboring methylene groups, exhibits a spacing ($\nu$=1210 cm$^{-1}$) which differs only little from the $CH_2$-bending frequency of the neutral molecule ($\nu$=1458 cm$^{-1}$) [6] -- again attesting to the essentially nonbonding character of the highest occupied orbital.

The second and third bands of the spectrum have been assigned to the $3b_2$ and $5a_1$ molecular orbitals, respectively. These two orbitals are derived from the $2e_u$ valence Walsh orbitals of

Fig. 1. The Photoelectron Spectrum of Oxetane.



cyclobutane. (Vide infra.) That they are both lower lying ($IE_2$=11.3 eV; $IE_3$=12.0 eV) than the degenerate pair of the carbocycle ($-\varepsilon$ =11.0 eV, the average energy of the Jahn-Teller-split components) reflects the influence of the more electronegative oxygen.

(The rest of the bands -- also assigned according to the calculations -- are not of particular interest here.)

The assigned ionization energies from the spectrum and MO calculations of oxetane, together with those reported for cyclobutane [1], can provide a correlation diagram for the observable orbitals ($IE < 21.21$ eV). (Figure 2)

Figure 2 reveals the most obvious perturbation effected by the oxygen to be a scrambling of the $\sigma/\pi$-ordering in oxetane, relative to the MO sequence in the parent hydrocarbon -- a result paralleling that found for cyclopropane and ethylene oxide. [7] Of greater consequence, however, is the perturbation of the high-lying $\sigma$-orbitals in cyclobutane to yield the $3b_2$ and $5a_1$ orbitals of oxetane. Figure 3 shows, that while these orbitals retain the basic form of their cyclobutane counterparts, the degeneracy has been lifted ($\Delta E$=0.7 eV), and the distribution of the wavefunctions over the four centers has been altered so as to localize the $a_1$ orbital in the vicinity of oxygen at the expense of the transannular carbon, and to localize the $b_2$ orbital in an exactly opposite manner. These two facets of the electronic structure of oxetane should have significant effects on the physical and chemical properties of its derivatives.

As mentioned above, one point of interest with regard to small ring compounds has been their

Fig. 2. Correlation of the Ionization Energies of Cyclobutane and Oxetane.

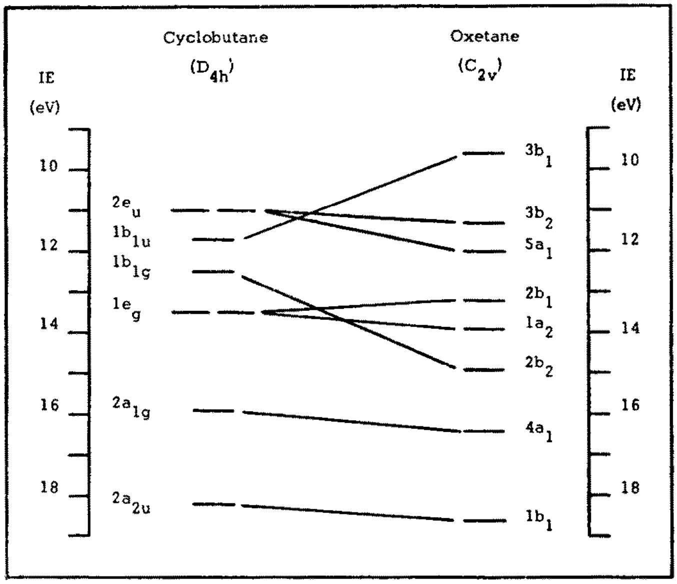
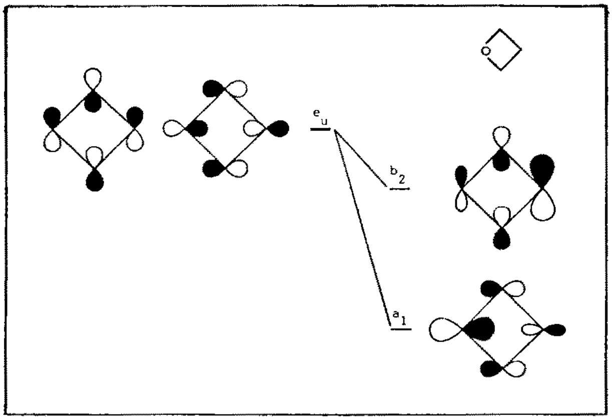


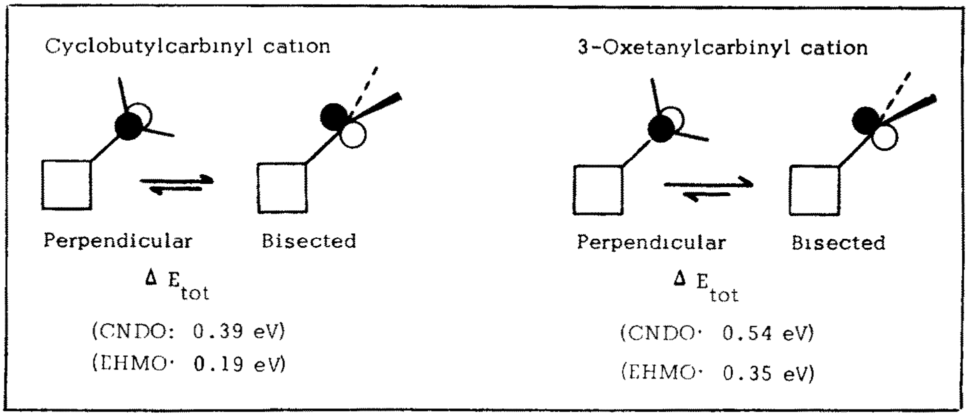
Fig. 3. The $e_u$ Orbitals of Cyclobutane and the Corresponding $3b_2$ and $5a_1$ Orbitals of Oxetane.



ability to provide conjugative interactions. Consider the cyclobutylcarbinyl and 3-oxetanylcarbinyl cations, each in its perpendicular and bisected conformations. (Figure 4) From the standpoint of overlap considerations, the $3b_2$ orbital, which stabilizes the bisected conformation, should interact more strongly in oxetane than it does in cyclobutyl; the $5a_1$ orbital which stabilizes the perpendicular conformation, should interact less strongly. In terms of energy matching, both oxetane orbitals should interact less strongly than the cyclobutane $e_u$ orbitals; however, the $b_2$ interaction will be greater than the interaction of the $a_1$ orbital. Thus, both energy and overlap factors should provide reinforcing effects serving to impart greater conformational preference in the case of the 3-oxetanylcarbinyl cation. Indeed, the calculations show the preference of this ion for the bisected conformation to be greater than that of the cyclobutyl analog by a factor of 1.5 - 2.0.

Oxetane's greater propensity for providing differentiating conjugation with sites adjacent to the ring might easily be tested by photoelectron spectroscopy. Thus, with 3-bromo-

Fig. 4. Calculated Conformational Preferences.



oxetane -- where the two π-type "lone pairs" of the halogen provide simultaneous cases of conjugation with the $3b_2$ and $5a_1$ ring orbitals -- one could expect to find greater differences in band shapes than have been observed for the bromine "lone pairs" in cyclobutyl bromide. [8] In addition, other manifestations of this property of oxetane might be found in the gas phase molecular geometries and solvolysis kinetics of various oxetanyl derivatives.

ACKNOWLEDGEMENT: The author would like to thank Prof. Dr. Hans Bock, who made his stay at the University of Frankfurt, Germany, where this work was begun. He so like to acknowledge the partial support of this work at Cornell by the National Science Foundation (GP 28137) and the National Institutes of Health (GM 13468).

## REFERENCES

1] P. Bischoff, E. Haselbach and E. Heilbronner, Angew. Chem. Int. Ed. Eng., 9, 953 (1970).
2] R. Hoffmann and R. Davidson, J. Amer. Chem. Soc., 93, 5699 (1971).
3] S. Chan, J. Zinn and W. Gwinn, J. Chem. Phys., 34, 1319 (1961).
4] See, for example, T. Ueda and T. Shimanouchi, J. Chem. Phys., 49, 470 (1968), and references therein.
5] G. Hernandez, J. Chem. Phys., 38, 2233 (1963).
6] R. Zürcher and H. Günthard, Helv. Chim. Acta, 38, 849 (1955).
7] H. Basch, M. Robin, N. Kuebler, C. Baker and D. Turner, J. Chem. Phys., 51, 52 (1969).
8] F. Brogli and E. Heilbronner, Helv. Chim. Acta, 54, 1423 (1971).