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Photoelectron Spectra of Tetrahydropyran, 1,3-Dioxane, and 1,4-Dioxane

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Photoelectron spectroscopy is useful for the study of electronic structures of molecules, in particular of occupied orbital energies of molecules. In this paper, we study the photoelectron spectra of such cyclic ethers as tetrahydropyran, 1,3-dioxane, and 1,4-dioxane, special attention being paid upon the interaction between oxygen lone pair orbitals in dioxanes which contain two oxygen atoms.

Experimental

Materials. Tetrahydropyran, 1,3-dioxane, and 1,4-dioxane were purified in usual ways and their purities were checked with gas chromatograms and NMR spectra.

Measurements. Photoelectron spectra (PES) were measured with a JASCO Model PE-1 photoelectron spectrometer by using the 584 Å helium resonance line as a light source.

Theoretical

The CNDO/2[1] calculation was carried out for the cyclic ethers under consideration by a FACOM 270—30 computer at the Institute of Physical and Chemical Research. The geometrical structure of 1,4-dioxane necessary for the calculation was taken from Ref. 2, and those of tetrahydropyran and 1,3-dioxane were properly assumed on the basis of the appropriate data given in Ref. 2. These compounds take a chair form at room temperature.[2–4]

Results and Discussion

PES of these cyclic ethers are shown in Fig. 1, and the vertical ionization potentials (Ip_v's) obtained from PES are summarized in Table 1. The observed orbital energies, ε_{obs}, estimated by Koopmans' theorem,[5] $\varepsilon_{obs} = -Ip_v$, are shown in Fig. 2a. In Fig. 2b, the orbital energies calculated by the CNDO/2 method, ε_{calc}'s, are shown for the purpose of comparison.

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[1] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

[2] "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, ed. by L. E. Sutton, The Chemical Society, London (1958); *ibid.*, No. 18 (1965).

[3] V. M. Rao and R. Kewley, *Can. J. Chem.*, **47**, 1289 (1969).

[4] H. M. Pickett and H. L. Strauss, *J. Amer. Chem. Soc.*, **92**, 7281 (1970).

[5] T. Koopmans, *Physica*, **1**, 104 (1934).

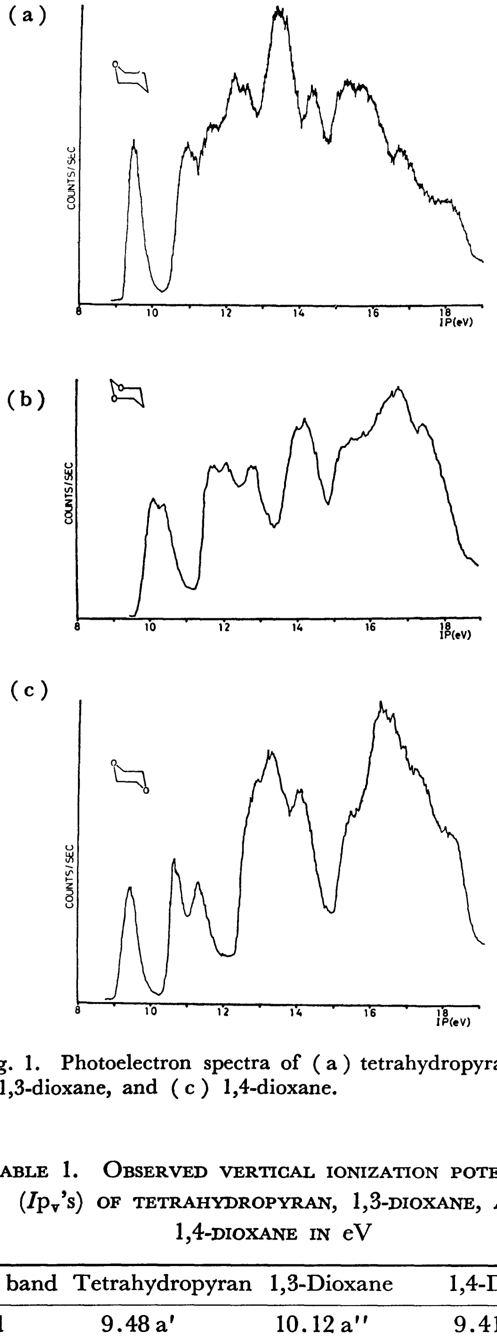

Fig. 1. Photoelectron spectra of (a) tetrahydropyran, (b) 1,3-dioxane, and (c) 1,4-dioxane.

Table 1. Observed vertical ionization potentials (Ip_v's) of tetrahydropyran, 1,3-dioxane, and 1,4-dioxane in eV

PES band	Tetrahydropyran	1,3-Dioxane	1,4-Dioxane
1	9.48 a'	10.12 a''	9.41 a_g
2	10.90 a'	10.38 a'	10.60 a_g
3	11.57 a''	11.66 a'	11.27 b_g
4	12.19	12.07	12.86
5	12.53	12.80	13.26
6	13.30 (broad)	14.00	13.60
7	14.28	14.17	14.06
8	15.23 (broad)	15.21 (broad)	15.40 (broad)

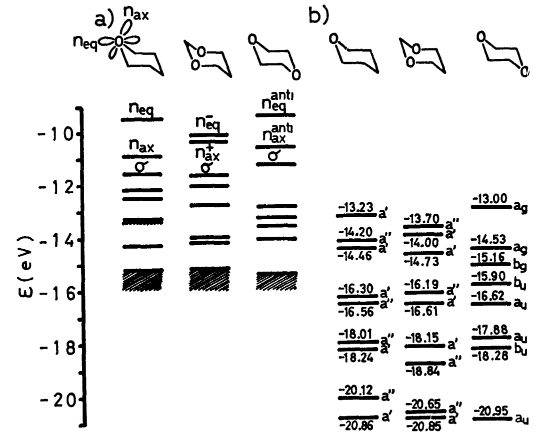

Fig. 2. Orbital energy diagrams.
a) The observed orbital energy diagram obtained on the assumption, $\varepsilon = -Ip_v$ (Koopmans' theorem).
b) The orbital energy diagram obtained by the CNDO/2 calculation.

Concerning the first Ip's of these compounds, the relative height of the calculated molecular orbitals reproduces quite well the observed tendency as clearly seen in Fig. 2. Therefore, we may assign the first Ip's of these compounds to the highest occupied orbitals given by the CNDO/2 calculations. That is to say, the first Ip's of tetrahydropyran, 1,3-dioxane, and 1,4-dioxane may be ascribed to the equatorial type lone pair (n_{eq}) orbital of the oxygen atom, to the antibonding combination of the two n_{eq} orbitals of the two oxygen atoms (n_{eq}^-), and the antiparallel type combination of the two n_{eq} orbitals of the two oxygen atoms (n_{eq}^{anti}), respectively.

Cradock and Whiteford[6] assigned the first (10.04 eV), second (11.91 eV), and third (13.43 eV) bands of methyl ether to b_1(n), a_1(n), and b_2(σ) from the analogy with the assignment on the water molecule.[7] The splitting between the two n orbitals is 1.87 eV for methyl ether. The corresponding three bands appear at 9.61, 11.08 (adiabatic) and 11.92 eV (adiabatic) for ethyl ether,[8] the splitting between the two n orbitals being 1.47 eV (adiabatic). These three bands correspond well in their positions to the lower energy three bands of tetrahydropyran at 9.48, 10.90, and 11.57 eV. This seems to mean that the second band of tetrahydropyran may be related with the non-bonding orbital.[9] According to this assignment, the splitting between the n_{eq} and n_{ax} orbitals is 1.42 eV.

The CNDO/2 calculation shows that the orbitals of 1,3-dioxane are ordered from the top as follows: n_{eq}^-, n_{ax}^+, σ, n_{ax}^-, σ, n_{eq}^+. The second highest occupied MO, n_{ax}^+, is represented by the bonding type combination of the two n_{ax} orbitals of the two oxygen atoms. The calculated energy difference between the n_{eq}^- and n_{ax}^+ orbitals (0.30 eV) corresponds well to the observed difference between the first and second bands (0.26 eV). This may support the assignment of the

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[6] S. Cradock and R. A. Whiteford, *J. Chem. Soc., Faraday Trans.* 2, **68**, 281 (1972).

[7] J. Dewiche, P. Natalis, and J. E. Collin, *Int. J. Mass Spec. Ion. Phys.*, **5**, 443 (1970).

[8] M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, **1964**, 4434.

[9] This assignment is reverse to the prediction from the CNDO/2 calculation. Since the observed splitting between the second and third orbitals is rather small for tetrahydropyran (0.67 eV), their orders may be difficult to be determined by the CNDO/2 calculation.

second band. According to the above-mentioned order of the orbitals, the observed fourth and sixth bands of 1,3-dioxane may tentatively be assigned to the n_{ax}^- and n_{eq}^+ orbitals, respectively, and the splittings between the n_{ax}^+, and n_{ax}^- orbitals and between the n_{eq}^- and n_{eq}^+ orbitals amount to 1.69 and 3.88 eV, respectively. The two n_{eq} orbitals of 1,3-dioxane may interact through space rather than through bond[10] because the overlap integral between them is not small, while the two n_{ax} orbitals may interact through bond rather than through space.

According to the CNDO/2 calculation shown in Fig. 2, the occupied MO's of 1,4-dioxane decrease their energies in the following order: $n_{eq}^{anti} > n_{ax}^{anti} > \sigma > n_{ax}^{para} > \sigma > \sigma > n_{eq}^{para}$. Here n_{ax}^{para} and n_{eq}^{para} mean the parallel type combinations of the two n_{ax} orbitals and of the two n_{eq} orbitals, respectively. According to this tentative assignment, the splittings between the n_{ax}^{anti} and n_{ax}^{para} orbitals and between the n_{eq}^{anti} and n_{eq}^{para} orbitals may become 2.26 eV and 4.65 eV, respectively. In 1,4-dioxane the interactions between the two n_{ax} orbitals as well as between the two n_{eq} orbitals may occur through bond rather than through space.

Recently Sweigart and Turner[11] reported the PES of these compounds and discussed the interaction between nonbonding orbitals belonging to two different oxygen atoms of each molecule. In their study, however, they did not make any theoretical calculation and did not consider the presence of the two types (equatorial and axial) of nonbonding orbitals on each oxygen atom of these compounds.

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[10] R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

[11] D. A. Sweigart and D. W. Turner, *ibid.*, **94**, 5599 (1972).