Ultraviolet Photoelectron Spectra of Crown Ethers

Masatsugu Kajitani, Akira Sugimori, Naoki Sato,† Kazuhiko Seki,†
Hiroo Inokuchi,† and Yoshiya Harada*,††
Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho, Chiyoda-ku, Tokyo 102
†Institute for Molecular Science, Myodaiji, Okazaki 444
††Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

(Received December 18, 1978)

The He I spectra of 12-crown-4, 15-crown-5, 18-crown-6, dicyclohexyl-18-crown-6, and dibenzo-18-crown-6 have been measured. The features of the spectra are similar except for the case of dibenzo-18-crown-6, where two lower IP bands correlated with the highest occupied π-orbitals of benzene are observed together with the bands due to the polyether ring. By the aid of the CNDO/2 calculation, the lower IP bands of the spectra have been assigned to the MO's mainly due to the equatorial or axial type non-bonding orbitals of the oxygen atoms of the polyether rings.

There has been considerable interest in macrocyclic "crown" ethers since Pedersen reported their syntheses in 1967.[1,2] They are capable of binding with a wide variety of salts to form complexes and can thereby solubilize many inorganic reagents in nonaqueous solvents, in which the reagents exhibit enhanced anion activity.[3,4] Thus, crown ethers have been found to be very useful reagents in organic chemistry. In life sciences, they are also used as models for carrier molecules in the study of cation transport through membranes.[5]

In order to study the electronic structure of crown ethers, we have measured the He I spectra of 12-crown-4 (I), 15-crown-5 (II), 18-crown-6 (III), dicyclohexyl-18-crown-6 (IV), and dibenzo-18-crown-6 (V) (Fig. 1), and tried to assign the observed bands with the aid of molecular orbital calculations.

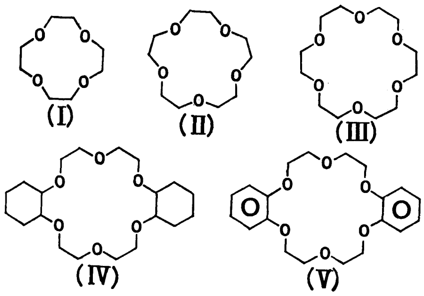

Fig. 1. Crown ethers.
(I) 12-Crown-4, (II) 15-crown-5, (III) 18-crown-6, (IV) dicyclohexyl-18-crown-6, (V) dibenzo-18-crown-6.

Experimental

Commercial crown ethers were purified by vacuum sublimation. He I spectra were recorded on a Perkin-Elmer PS-18 photoelectron spectrometer using the Ar and Xe doublets as internal standards. The resolution was less than 30 meV. The spectra of I and II were measured at room temperature, and those of the larger crown ethers at 70 °C (III), 150 °C (IV), and 190 °C (V).

Results and Discussion

Figure 2 shows the He I spectrum of 12-crown-4. Four broad peaks appear around 9.3, 9.9, 11.4, and 12.5 eV. In the higher IP region the spectrum is diffuse, as is frequently the case in large molecules.

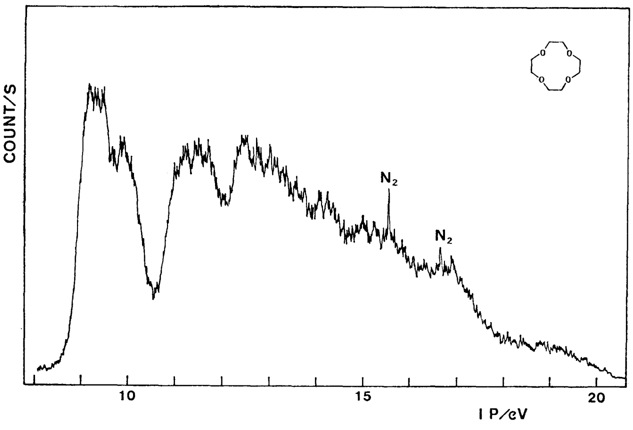

Fig. 2. He I spectrum of 12-crown-4.

The molecular structure of 12-crown-4 has not been determined experimentally. Pullman *et al.*[5] calculated the energies of two types of conformations, maxidentate (crown) and alternate forms (Fig. 3), using an *ab initio* LCAO MO method. According to them, the most stable conformer is a deformed alternate one; the value of its torsion angle τ about the C_2C_3 bond is 70°, while the symmetric alternate conformer (Fig. 3) has $\tau=48.65°$. We calculated the molecular orbitals of these alternate conformers by the CNDO/2 method. The energies of the upper occupied levels and the shapes of the corresponding wave functions are illustrated schematically in Fig. 4. The symmetric alternate conformer

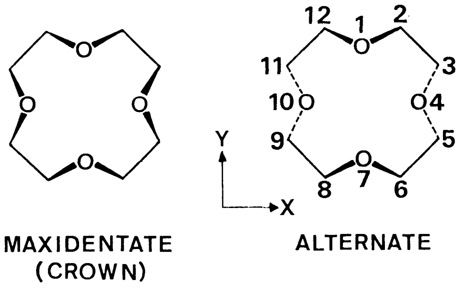

Fig. 3. Conformations of 12-crown-4. All the carbon atoms lie on the same plane.

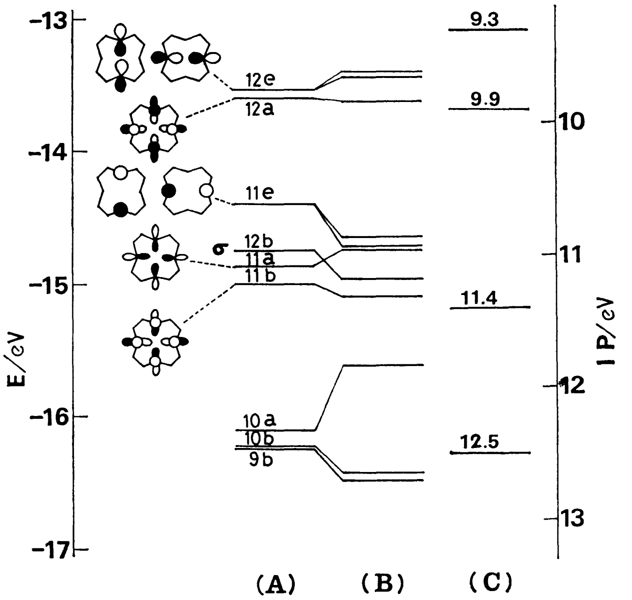

Fig. 4. The energies of the upper occupied levels and the shapes of the corresponding wave functions of 12-crown-4.
(A) Calculated energies for the symmetric alternate conformer. (B) Calculated energies for the most stable conformer. (C) Observed IP values (peak positions in the spectrum).

belongs to the symmetry group S_4, having degenerate e orbitals, whereas the degeneracy is lifted in the stable one. The CNDO/2 calculation shows that the highest occupied e orbitals of the symmetric conformer (12e in Fig. 4) are mainly due to the non-bonding combination of the equatorial type lone pair orbitals (N_{eq}) of two oxygen atoms and the second highest (12a) to the bonding combination of four N_{eq} orbitals together with the anti-bonding combination of four axial type lone pair orbitals (N_{ax}). For the deformed form, the splitting of the 12e orbital is calculated to be only 0.04 eV (Fig. 4). Therefore, they may not be resolved in the observed photoelectron spectrum. Since the integrated intensity of the first (9.3 eV) band of 12-crown-4 is about twice as large as that of the second (9.9 eV) one, the first and second bands can be assigned to the 12e and 12a orbitals, respectively. Both these orbitals are due to lone pair type orbitals of oxygen atoms, having a similar localized nature. Thus the intensity ratio of the two bands due to the 12e and 12a orbitals can be expected to be 2 to 1, the ratio of their degeneracies.** Further, the assignment of the second band to the 12a orbital can be supported from a comparison of the spectrum of 12-crown-4 with spectra of the other crown ethers (see below). The intensity of the 11.4 eV band, as compared to those of the first and second bands, suggests that it corresponds to the removal of electrons from two or three occupied orbitals. Judging from the results of the calculation shown in Fig. 4, electrons from the 11e orbital, the anti-bonding combination of two N_{ax} orbitals, may contribute to this band.

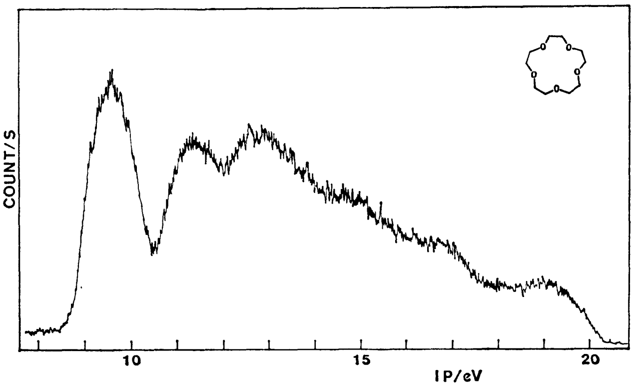

Fig. 5. He I spectrum of 15-crown-5.

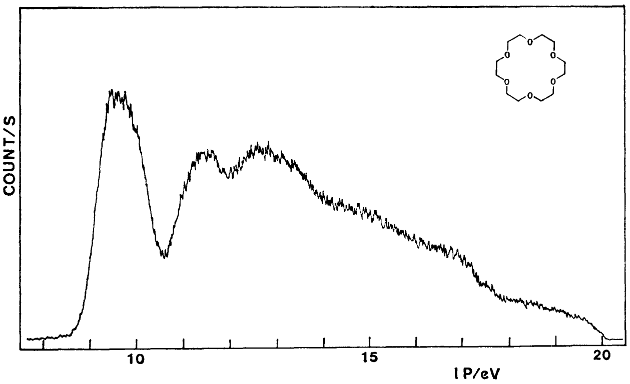

Fig. 6. He I spectrum of 18-crown-6.

Figures 5 and 6 show the He I spectra of 15-crown-5 and 18-crown-6, respectively. The appearance of the spectra is similar to that of 12-crown-4 (Fig. 2), except for the portion of the spectra between 8.5 and 10.5 eV. In the former spectra the 9.3 and 9.9 eV bands of 12-crown-4 appear to be mixed into one band located at intermediate positions: 9.58 eV for 15-crown-5 and 9.7 eV for 18-crown-6. This can be interpreted by assuming that orbitals having shapes similar to those of the 12e and 12a of 12-crown-4 are responsible for the first band in its higher homologs. Since 12e type orbitals due to anti-bonding combinations of N_{eq}'s become more stable and 12a type orbitals due to bonding combination of N_{eq}'s become less stable with increasing ring size of polyethers, the bands due to these two orbitals may not be resolved for 15-crown-5 and 18-crown-6. As for the second bands in Figs. 5 and 6, the peak positions (11.4 eV for 15-crown-5, 11.5 eV for 18-crown-6) are nearly the same as that in 12-crown-4. This is considered to be consistent with the previous assignment that the 11.4 eV band in 12-crown-4 is related to the 11e orbital, since the energy of the 11e type orbitals may not shift much with increasing ring size owing to the small interaction among N_{ax} orbitals.

** A similar intensity relation has been found in the photoelectron spectrum of biphenyl, in which the lowest three ionization bands are associated with the highest occupied π-orbitals of the benzene rings (J. P. Maier and D. W. Turner, *Faraday Discuss. Chem. Soc.*, **54**, 149 (1972)). The intensity ratio of approximately 1 : 2 : 1 has been observed for these three bands, of which the second one is due to almost doubly degenerate orbitals.

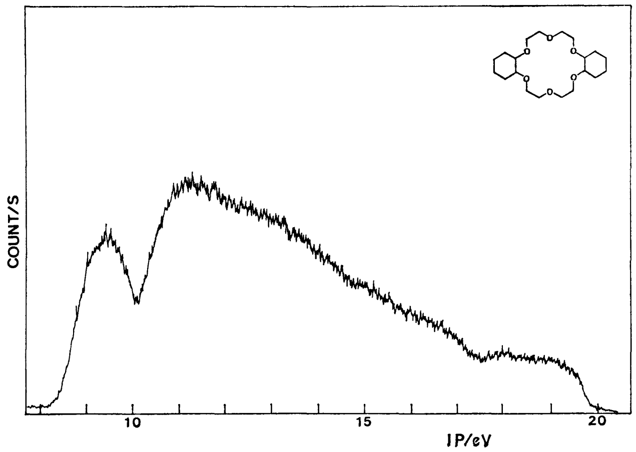

Fig. 7. He I spectrum of dicyclohexyl-18-crown-6.

Figure 7 shows the He I spectrum of dicyclohexyl-18-crown-6. With the introduction of two cyclohexane rings, the peak position of its first band (9.45 eV) is lowered by 0.25 eV as compared with that of 18-crown-6. Furthermore, in the 10—13 eV region the feature of the spectrum is different from those of the spectra of unsubstituted crown ethers. This may be due to the effect of the σ-orbitals of cyclohexane, the adiabatic IP of which is around 10.0 eV.[6]

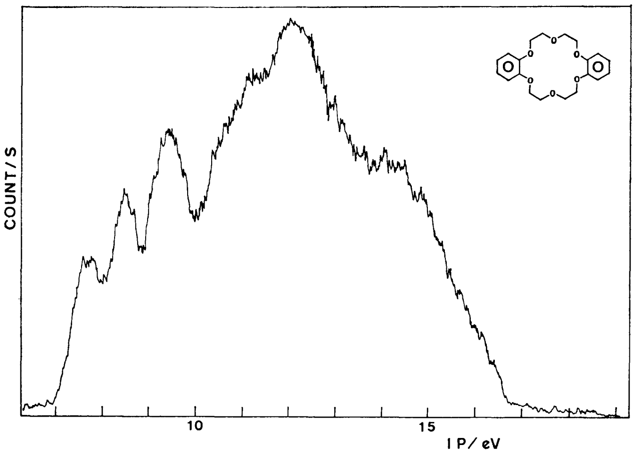

Fig. 8. He I spectrum of dibenzo-18-crown-6.

The He I spectrum of dibenzo-18-crown-6 is shown in Fig. 8. The third band located at 9.45 eV can be correlated to the first band of 18-crown-6. The first and second bands (vertical IP 7.70 eV, 8.50 eV) may be related to electrons from the highest occupied doubly degenerate π-orbitals (e_{1g}) of benzene rings. This assignment is supported by the fact that the *o*-dimethoxybenzene gives the first and second bands at vertical IP 8.20 and 8.91 eV,[7] which are associated with the e_{1g} orbitals of the benzene ring. Since there is interaction in this molecule, among the e_{1g} orbitals of the benzene ring (IP 9.24 eV for benzene) and the non-bonding orbitals of the oxygen atoms (IP 10.96 eV for methanol), the former orbitals are considered to split and give two bands in the lower IP region of the spectrum.*** The vertical IP's relating to these bands are further lowered by 0.4—0.5 eV for dibenzo-18-crown-6, where the π-conjugated system is larger than that of *o*-dimethoxybenzene.

As for the IP region higher than 10 eV the appearance of the spectrum in dibenzo-18-crown-6 is quite different from that of 18-crown-6 owing to the introduction of two benzene rings. However, the shoulder at 11.2 eV may be correlated to the second band of 18-crown-6.

The authors wish to thank Prof. A. Pullman, Institut de Biologie Physico-Chimique, C. N. R. S., for sending them the data on the atomic cordinates of the most stable conformer for 12-crown-4.

References

1) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 2495 (1967).
2) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
3) J. J. Cristensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).
4) A. C. Knipe, *J. Chem. Educ.*, **53**, 618 (1976).
5) A. Pullman, C. Giessner-prettre, and Yu. Y. Kruglyak, *Chem. Phys. Lett.*, **35**, 156 (1975).
6) A. W. Potts and D. G. Streets, *J. Chem. Soc., Faraday Trans. 2*, **70**, 875 (1974).
7) N. Sato, unpublished results.

*** We can correlate the 8.20 and 8.91 eV bands of *o*-dimethoxybenzene with the π_2 and π_3 orbitals of the benzene ring, respectively, because, in *o*-dimethoxybenzene, the π_2 orbital of the ring having its maximun electron density at both points of substitution is more affected than the π_3 orbital.