BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 278—279 (1970)

On the Nature of the First Ionization Potential of Tropolone

Pill-Soon Song and Michael A. Latino

Department of Chemistry, Texas Technological University, Lubbock, Texas 79409, U. S. A.

(Received June 6, 1969)

Information concerning ionization potentials of molecules provides an important clue to their electronic states. An interesting question as to the nature of the first ionization potential of tropolone is whether the first ionization potential represents energy to remove an electron from the non-bonding orbital on oxygen or from a π-molecular orbital. Higasi *et al.* measured the first ionization potentials of tropolone and related molecules.[1] They measured the ionization potential (vertical) of tropolone mass spectrometrically using two different methods of evaluation; namely, 9.86 eV by the critical slope method and 9.83 eV by the linear extrapolation method. The ionization has been interpreted to originate from the nonbonding electron orbital on the carbonyl oxygen. Higasi *et al.* concluded that the higher ionization potential of tropolone than tropone is then, due to the intramolecular hydrogen bonding in the former. On the other hand, the lower ionization potential (9.43 eV) of 2-amino tropone than tropolone is interpreted as being due to weaker hydrogen bonding. However, they have not ruled out a possibility of the π-electron ionization potential being the lowest. This Note is concerned with that last point.

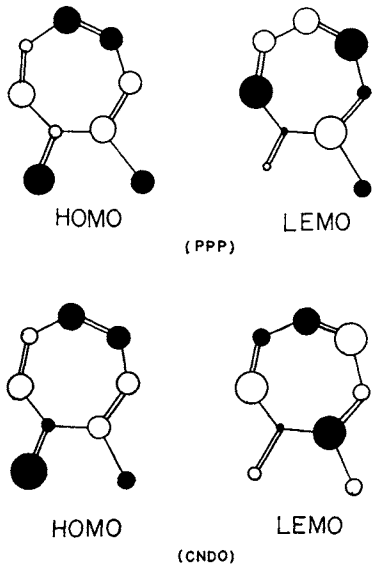

Fig. 1. Wavefunctions of the highest occupied (HOMO) and lowest empty (LEMO) molecular orbitals of tropolone calculated by the PPP and CNDO methods. The dark and open circles represent plus and minus signs, respectively, and the radius indicates an approximate magnitude of the LCAO coefficients.

The symmetry of the highest occupied (HOMO) and lowest empty (LEMO) MOs is of interest to characterize excitation and ionization processes in the molecule. Figure 1 shows HOMO and LEMO obtained from PPP SCF MO[2,3] and CNDO/2 SCF MO[4] computations.[2-4] It turns out that both HOMO and LEMO are of π-orbital origin. The HOMOs from PPP and CNDO appear to be in close agreement. Our calculations using both methods, therefore, suggest that the lowest ionization potential is due to the ionization of π-electron. If we apply Koopmans' theorem, we obtain the first ionization potentials of 8.75 eV (π, PPP) and 9.93 eV (π, CNDO) for tropolone. Furthermore, the molecular orbital of non-bonding character (63% of the MO is made up of the carbonyl oxygen nonbonding orbitals) is predicted to have an energy significantly lower (by 2.4 eV) than the HOMO shown in Fig. 1. This would qualitatively mean that the second ionization potential may be of the nonbonding origin. Numerical agreement between the CNDO-calculated and experimental ionization potentials of tropolone may be fortuitous since Koopmans' theorem ionization potentials are frequently higher than observed values. Furthermore, CNDO tends to yield poor eigenvalues.[5] Nevertheless, relative ordering of the π- and σ-HOMOs with an energy gap of 2.4 eV appears to be sufficiently large to warrant further experimental investigations of ionization potentials of tropolone and substituted tropolone series. It has been observed that CNDO correclty predicted the first ionization potential of pyridine being of σ-type, although the same method failed to predict the

1) K. Higasi, T. Nozoe and I. Omura, This Bulletin, **30**, 408 (1957).

2) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

3) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

4) J. A. Pople and G. A. Segal, *J. Chem. Soc.*, **1966**, 3289.

5) J. E. Bloor and D. L. Breen, *J. Amer. Chem. Soc.*, **89**, 6835 (1967).

observed ordering of the two types of ionization potentials for pyrazine in which the energy difference is rather small.[5] In the present case, the energy spacing of 2.4 eV is sufficiently large.

In connection with our prediction discussed above, it is useful to describe ionization potentials of related molecules. Tropilidene(cycloheptatriene) has an ionization potential of 8.55 eV.[6] Obviously, the ionization potential here is π-type. It is therefore an interesting question whether the carbonyl group in tropone lowers the π-HOMO energy of the seven-membered ring system sufficiently to place it below the nonbonding level. The interpretation given by Higasi *et al.*[1] implies such a situation. The ionization potential of 2-amino tropone is lower than that of tropone and tropolone.[1] Higasi *et al.* interpret this trend to be due to weaker intramolecular hydrogen bonding in 2-amino tropone than in tropolone. However, since substituent effects on ionization potential of non-bonding electron are relatively small,[7] there exists a possibility that the lowering of the ionization potential of tropone by 2-amino substitution reflects the π-electron ionization process. Further experimental and theoretical investigations are certainly warranted to establish the nature of the ionization process in tropolone series.

This work (Electronic Structures and Spectra of Some Natural Products of Theoretical Interest. II.) was supported by the National Science Foundation) (Grant No. GB-8055) and the Robert A. Welch Foundation (Grant No. D-182). One of the authors(MAL) would like to thank NASA for a predoctoral fellowship (1966—1968). The computational assistance by the staff of the Texas Technological University computer center is greatly appreciated.

6) A. G. Harrison, L. R. Honnen, J. J. Dauben, Jr., and F. P. Lossing, *J. Amer. Chem. Soc.*, **82**, 5593 (1960).

7) K. Higasi, I. Omura and H. Baba, *J. Chem. Phys.*, **24**, 623 (1956).