

THE HE(I) PHOTOELECTRON SPECTRA OF XYLEMES AND METACYCLOPHANES.

A REASSIGNMENT OF THE LOWEST IONIC STATE OF [2.2]METACYCLOPHANE.

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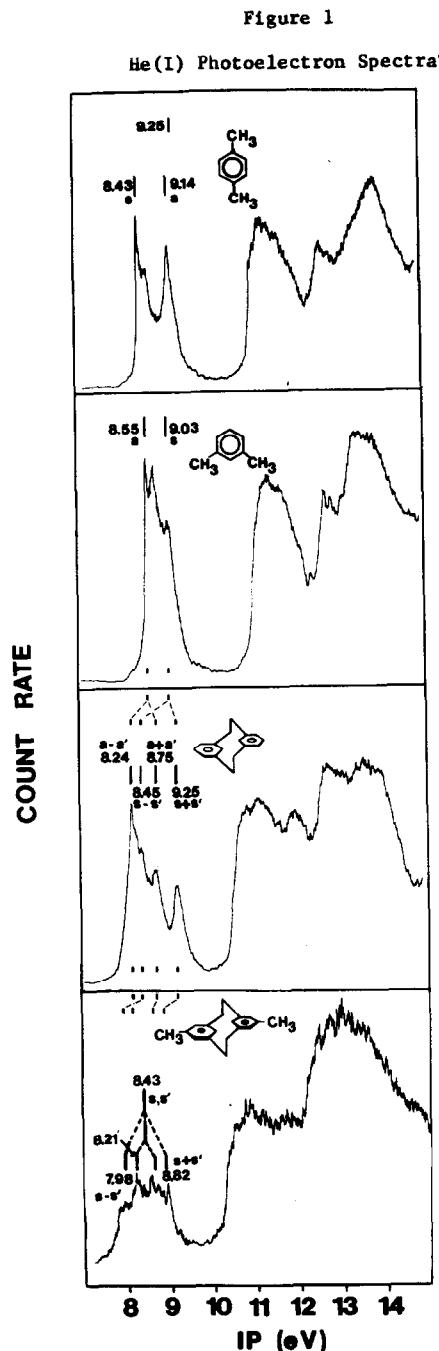
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We wish to report the results of our analysis of the He(I) photoelectron spectra of meta- and para-xylene, [2.2]metacyclopahane, 1 and its 5,13-dimethyl derivative, 2.¹ This analysis leads to a different assignment of the first band for the parent metacyclopahane, different vertical ionization potentials for the first ionic states of the xylenes and a different interpretation of the origin of the methyl shift than previous work would imply.^{2,3}

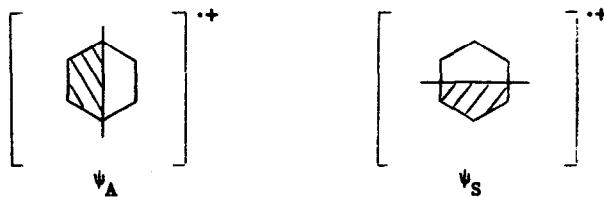
The experimental spectra (Figure 1) were obtained using a Perkin Elmer PS-18 photoelectron spectrometer calibrated against argon-xenon mixtures. The preparation of the 5,13-dimethyl-metacyclopahane has been described previously.^{1,4} The [2.2]metacyclopahane was prepared by the method of Allinger.⁵

The gross features of our xylene spectra are similar to those of Klessinger.³ However, the O-O vibrational bands appear to be of maximum intensity ($\nu \approx 1600\text{cm}^{-1}$) which leads to reductions in the vertical ionization potentials compared to those estimated from the previous work.³ The increased resolution of the present spectra argues in favor of the present estimates of the vertical ionization potentials.

The basis of our assignment of the first band in the spectrum of [2.2]metacyclopahane comes from comparison with the dimethyl derivative and the shifts expected for methyl substitution. We quantify the methyl shift from the experimental spectra of benzene versus toluene and mesitylene¹ versus meta-xylene. In these cases the positions of the first two bands can be considered to be the result of the interaction of the methyl substituents with symmetric (ψ_S) or antisymmetric (ψ_A) arene ion structures. For the benzene-toluene pair, the methyl pseudo Π group interaction⁶ lifts the degeneracy (~9.25 eV in benzene) of these two states with the



a) Spectra of the metacyclophanes were recorded at elevated ($\sim 50-100^\circ\text{C}$) temperature using a Perkin Elmer PS-18 Spectrometer.



ψ_S band maximum at 8.82 eV and the ψ_A band maximum at 9.3 eV. The methyl shift (~ 0.43 eV) is thus symmetry selective. The spectra of mesitylene and meta-xylene can be compared in the reverse sense in that the two states (A and S) are degenerate (~ 8.42 eV) in mesitylene. Removal of one of the methyl groups lifts the degeneracy and the antisymmetric state is assigned the first ionization potential of meta-xylene (ψ_A , 8.55 eV). The second band corresponds to the symmetric structure (ψ_S , 9.03 eV). The methyl shift in this case is 0.61 eV. The discrepancy between the two estimates of the methyl shift can be explained by Jahn-Teller effects which would lead to an underestimate for the benzene-toluene comparison and an overestimate for the mesitylene-meta-xylene comparison. The effective methyl shift is therefore taken as the average (0.52 eV).

The metacyclophanes show four states corresponding to ionization potentials of less than 10 eV. These arise from antisymmetric ($\psi_S - \psi_S$, $\psi_A - \psi_A$) and symmetric ($\psi_S + \psi_S$, $\psi_A + \psi_A$) combinations of the ψ_S and ψ_A structural pairs. The 5,13-dimethyl compound shows a splitting pattern expected from large interaction between ψ_S , ψ_S , and a smaller interaction between ψ_A , ψ_A , giving the order $\psi_S - \psi_S$, (7.98 eV), $\psi_A - \psi_A$, (8.21 eV), $\psi_A + \psi_A$, (8.7 eV) and $\psi_S + \psi_S$, (8.82 eV). The effect of removing both the 5 and 13 methyl groups should give rise to a shift of +0.52 eV on the two combinations of symmetric (ψ_S) basis structures leaving the combinations of antisymmetric basis structures (ψ_A) unchanged. The parent metacyclophane is thus predicted to have band maxima at 8.21 eV ($\psi_A - \psi_A$, obs. 8.24 eV), 8.50 eV ($\psi_S - \psi_S$, obs. 8.45 eV), 8.7 ($\psi_A + \psi_A$, obs. 8.75 eV) and 9.34 eV ($\psi_S + \psi_S$, obs. 9.25 eV). The most serious discrepancy is the fourth band which should be lowered by interaction with the totally symmetric Π structures which has been neglected here.

We believe the present assignment is preferable in that it does not require any sudden increase in the interring interaction constant as was necessitated by the previous one.² The chemical reactions of the metacyclophanes, which lead to ring closure, are adiabatic and must occur in spite of, rather than because of the nature of the lowest vertical ionic state.

Figure 2 shows a schematic representation of the positioning of potential surfaces required to accommodate both the pes and the chemical reactivity data. The vertical and adiabatic ground states may differ substantially.

Finally, we wish to emphasize⁶ that the methyl shift can be derived from the spectrum of 1,4-cyclohexadiene where hyperconjugation is demanded to explain the assignment of the first band. The shift⁶ from 9.25 eV, for ψ_5 interacting with the pseudo Π representation of a methyl group, is 0.41 eV using the interaction constant derived from the cyclohexadiene spectrum. We consider the methyl shift to be of hyperconjugative rather than inductive³ nature.

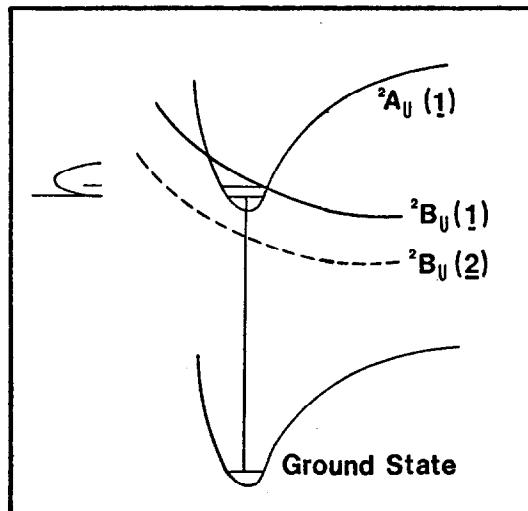


FIGURE 2
Schematic Potential Surface For [2.2]Metacyclophane Closure⁷

References

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7. The abissa represents the geometrical changes for formation of the $C_{15}-C_{16}$ bond of the pyrene system. The inset at the top left shows the implied vibrational structure of the 2A_u state and the diffuse character of the 2B_u state.