

ORBITAL INTERACTION IN 2a,8b-DIHYDROCYCLOPENT[cd]AZULENE

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In a recent communication, one of our research groups described the successful synthesis of a number of annelated semibullvalenes¹ In particular, we noted that 2,8-bridging of the semibullvalene nucleus with a butadiene moiety gives rise to a neutral hydrocarbon (1) which is (clearly) devoid of cyclopropane character and (less evidently) characterized by homoaromatic delocalization of its ten peripheral electrons. We now show that the UV photoelectron spectrum of 1 and semiempirical molecular orbital calculations support the earlier conclusions concerning the unique electronic properties of 1.

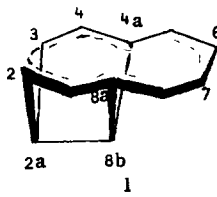


Figure 1 gives the photoelectron spectrum of 1 taken on a Vacuum Generators ESCA-2 spectrometer using HeI discharge radiation and operating at a resolution of 40 meV. The structure of the spectrum is remarkably similar to that of naphthalene and other 10π aromatic systems in that four distinct bands with large separations are evident in the region from 7-11 eV.² In view of the intensity and line width of these bands and in line with recent work on semibullvalene,³ these ionization potentials are assigned to four nondegenerate π levels.

To interpret the photoelectron results, extended Hückel (EHT) and perturbation molecular orbital (PMO) calculations have been performed using two model structures. Model 1 consists of a 'classical' semibullvalene in which a butadiene chain spans carbons 4a and 8a in sp^3

fashion.⁴ Model 2 differs from the first model in that all nonbridgehead atoms are confined to a common plane and thus corresponds to a structure with maximum π overlap.

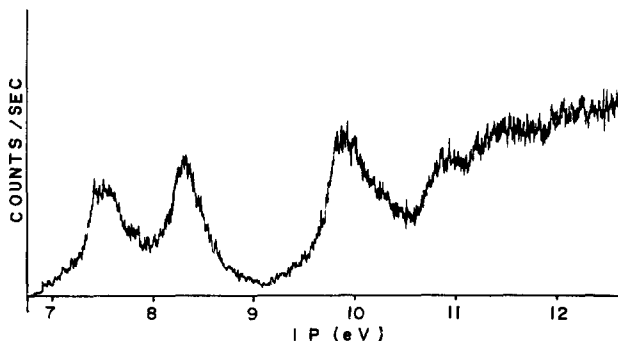


Figure 1 HeI Photoelectron Spectrum of 1

Results of the EHT calculations given in Figure 2 are significant in that they show the first three levels of the classical structure lie close together presumably due to σ - π mixing and that this interaction is significantly reduced in passing to the planar structure. While EHT calculations are known to reproduce absolute orbital energies poorly, the observed ordering of orbitals is generally in good agreement with the photoelectron results with experimental splittings between orbital levels being approximately 1.5 times larger than those calculated.^{5,6} With this in mind, the experimental ionization potentials are seen to agree best with those predicted for a planar structure in that the ratio $(\pi_3 - \pi_2)/(\pi_2 - \pi_1)$ found experimentally (1.8) is in good agreement with the value (1.5) predicted by Model 2.

FMO calculations support our conclusion that a localized non-planar π system does not adequately explain the molecular orbital properties of 1. Figure 3 gives the ionization potentials predicted by a 'molecule in a molecule' model in which we construct the π levels of 1 from the interaction of olefinic and Walsh e type cyclopropane orbitals. These calculations were done using the ionization potentials of cyclopropane,⁵ *cis*-butadiene,⁷ and 'pentadiene',⁵ as basis orbitals and an interaction integral β of -1.9 eV.⁵ Again the large splittings observed experimentally between π levels are not reproduced by calculations in which we regard 1 as being formed from cyclopropane and olefin fragments. Changes in the basis IP's or variation of the π overlap between C_3 and C_2 does not effect any better agreement.

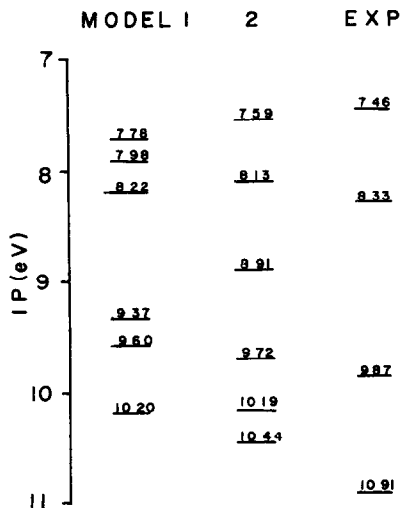
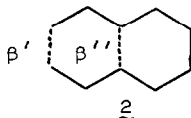


Figure 2 Comparison of π ionization potentials predicted by extended Hückel calculations for model structures 1 and 2 with experimental values. An energy zero of 4 eV has been used for the EHT results.

Since calculations of this kind have been successful at predicting the ionization potentials of semibullvalene and related systems to within 0.2 eV, the lack of agreement in this case means that the basis orbitals used for 1 are incorrect. Since the multiplicity and small separations between energy levels in the PMO calculations are due essentially to the twofold degeneracy of the centrally positioned Walsh orbitals, we interpret the results in Figure 3 as indicating that 1 has little cyclopropane character. This would be consistent with this molecule achieving a more planar structure (resulting in a lifting of the degeneracy of the Walsh e orbitals) and with existing pmr¹ and cmr⁸ data for 1.

Using a 10π model 2 in which β' and β'' are treated as variable,⁹ we find that the ex-



perimental ionization potentials correlate best with Hückel calculations in which $\beta' \approx \beta'' \approx -2.0$ eV thus indicating considerable delocalization. All of the combined evidence indicates, therefore, that 1 exists in a mesovalent form and is consequently a neutral homoaromatic

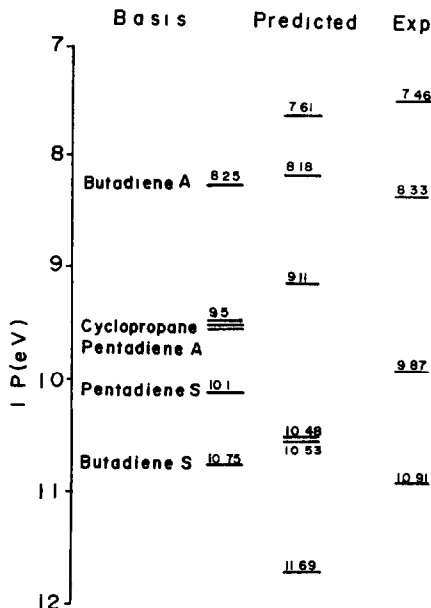


Figure 3 Comparison of the data derived from perturbation molecular orbital (PMO) calculations with experimental values. Levels are labeled with respect to the plane of symmetry in 1. Cyclopropane Walsh orbitals are doubly degenerate with one being of A and the other of S symmetry.

molecule.

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References

1. L.A. Paquette, R.E. Wingard, Jr., and R.K. Russell, *J. Amer. Chem. Soc.*, 94, 4739 (1972).
2. J.H.D. Eland and C.J. Danby, *Z. Naturforsch.*, 23a, 355 (1968)
3. R. Askani, R. Gleiter, E. Heilbronner, V. Hornung, and H. Musso, *Tetrahedron Letters*, 4461 (1971).
4. Y.C. Wang and S.H. Bauer, *J. Amer. Chem. Soc.*, 94, 5651 (1972)
5. P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, and G. Schröder, *Helv. Chim. Acta.*, 53, 1645 (1970)
6. G.P. Ceasar, W.E. Hall, and D.G. Streets, *Chem. Phys. Letters*, 17, 90 (1972)
7. P. Bischof and E. Heilbronner, *Helv. Chim. Acta.*, 53, 1677 (1970)
8. E. Wenkert, E.W. Hagaman, L.A. Paquette, R.E. Wingard, Jr., and R.K. Russell, *JCS Chem. Commun.*, in press
9. Simple Huckel calculations have previously been correlated with experiment IP's for 10π systems and show that $\alpha = -6.3$ eV and $\beta = -2.4$ eV for a hydrocarbon like 1. See ref. 2 and R. Boschi, W. Schmidt, J.-C. Gfeller, *Tetrahedron Letters*, 4107 (1972)