Tetrahedron Letters No. 46, pp 4461 - 4466, 1971. Pergamon Press. Printed in Great Britain.

THE ORBITAL SEQUENCE IN SEMIBULLVALENE, BARBARALENE AND DIHYDROBULLVALENE (1)

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(Received in UK 11 October 1971; accepted for publication 15 October 1971)

Some time ago we proposed a correlation diagram for the orbitals of bullvalene (I), dihydrobullvalene (II), tetrahydrobullvalene (V) and hexahydrobullvalene (2). We wish to show that the photoelectron spectra (P.E.-spectra) of barbaralene (III)(3), semibullvalene (IV(H))(4) and its dimethyl-derivative (IV(CH_3))(4) support this assignment. Figures 1 and 2 summarize the experimental results (5) and the correlation we propose. The vertical ionization potentials $I_{v,J}$ are given as orbital energies $\varepsilon_J = -I_{v,J}$ (Koopmans' theorem (6)) and have been rounded to the nearest 0.1 eV.

Comments on Figure 1

1) Column d contains the orbital energies $A(\pi) = -10.0$ eV and $A(e_S) = A(e_A) = -10.7$ eV, which have been assigned to the basis π-orbital $\pi = (2p_a+2p_b)/\sqrt{2}$ and to the basis Walsh-orbitals (7) $e_S = (2p_d-2p_e)/\sqrt{2}$, $e_A = (2\cdot 2p_c-2p_d-2p_e)/\sqrt{6}$ (cf. ref (2)) of vinyl-cyclopropane (VII). This basis is used for a qualitative description of the three highest occupied molecular orbitals of VII (8). The

basis orbital energies have been obtained by lowering the values derived from the P.E.-spectra of propene ($I_V(\pi)$ = 9.7 eV) and methyl-cyclopropane (8) (center of split band at 10.4 eV) by -0.3 eV to account for the inductive (?) stabilization of the basis orbitals (π, Walsh), which has been observed (2) to accompany the replacement of a methyl (or alkyl) group by a vinyl or cyclopropyl substituent.

2) Conjugation between π and e_A is described by a resonance integral $\beta_{ac} = \langle 2p_a|\mathcal{H}|2p_c\rangle = -2.2$ eV (2). For VII in its preferred bisected conformation one obtains the orbital energies $\varepsilon(\pi-\lambda e_A) = -9.1$ eV, $\varepsilon(e_S) = -10.7$ and $\varepsilon(e_A+\lambda\pi) = -11.7$ eV with $\lambda = 0.7_5$, in complete agreement with the experimental values given in column c.

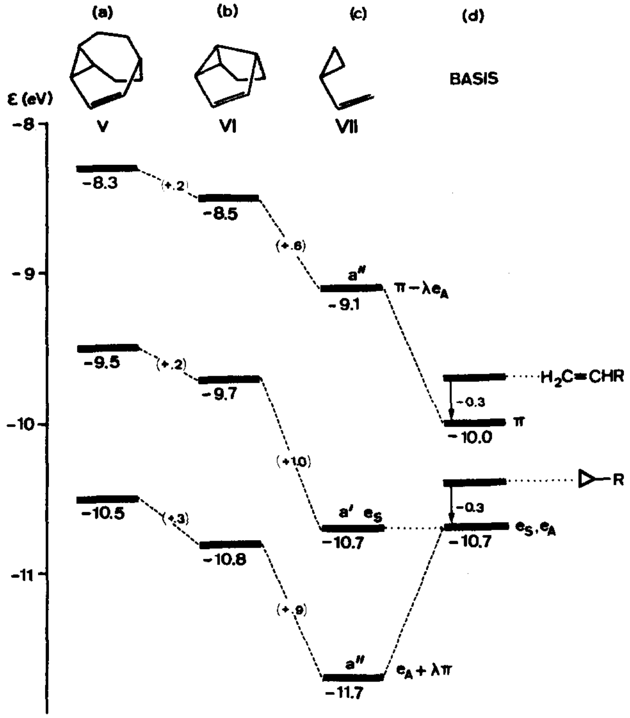

Fig. 1. Correlation diagram between the experimentally determined orbital energies of V-VII (column a - c). Column d shows the basis orbital energies of vinyl-cyclopropane.

3) Comparing VI and VII, the observed differences of corresponding orbital energies (values in brackets) are those expected for the influence of the bridging alkyl moiety in VI which contributes two additional substituents to the cyclopropane ring, but only one to the double bond. Note that the orbital $(e_A+\lambda\pi)$ shifted by 1.0 eV has more "Walsh-character" than $(\pi-\lambda e_A)$, shifted by only 0.6 eV.

4) Finally, insertion of two methylene groups into VI, yielding V, induces additional positive shifts of +0.2 to +0.3 eV.

Comments on Figure 2

1) Formulae 3 and 4 of ref. (2) yield the basis orbital energies $A(\pi) = -9.6$ eV and $A(e_S) = A(e_A) = -9.9$ eV for the non-interacting π- and Walsh-orbitals in II (column a). Allowing for the through space and through bond interaction (9) among the π basis orbitals of the two double bonds yields $\varepsilon(a''(\pi)) = -9.3$ eV and $\varepsilon(a'(\pi)) = -9.9$ eV (column b). Here and in the following we assume that II, III and IV(R) belong to the symmetry group C_S.

2) As shown previously (2) conjugation between e_S and $a'(\pi)$ and between e_A and $a''(\pi)$ leads to orbital energies for the four highest occupied molecular orbitals of II, which suggest the assignment shown in column c.

3) The results given in figure 1 indicate that the energies of the basis orbitals to be used for IV(H) are $A(\pi) = -9.8$ eV and $A(e_S) = A(e_A) \approx -10.1$ to -10.4 eV (column g). As expected these values are lower by 0.2 to 0.4 eV than those derived for II.

4) Qualitatively, conjugation between the π- and Walsh-orbitals of IV(H) must again lead to the same ordering of the highest occupied molecular orbitals as in the case of II. This is also the conclusion reached on the basis of Extended Hückel calculations (10)(11). The essential correctness of these predictions is strongly supported by the observed close resemblance of the P.E.-spectra of II and IV(H) and of the spectrum of the intermediate hydrocarbon III.

5) Along the series II→III→IV(H), the center of gravity of the four highest occupied orbitals shifts towards lower energies, as expected from the trend in the energies of the basis orbitals.

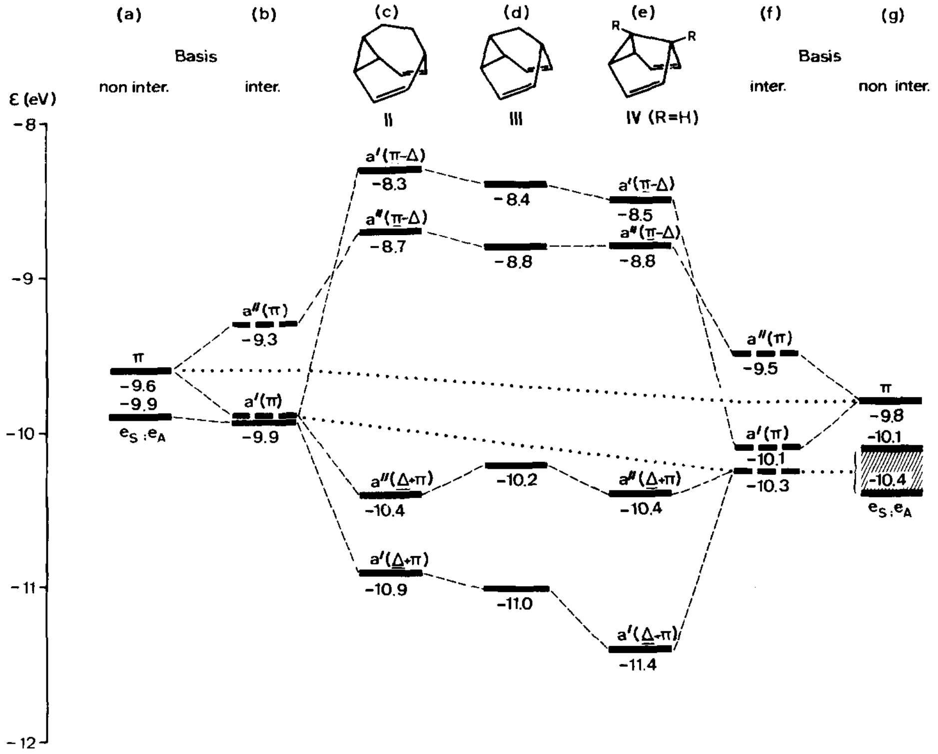

Fig. 2. Correlation diagram between the measured vertical ionization potentials of II - IV(H) (column c - e). The dominating π- or Walsh(Δ)-character of an orbital is indicated by underlining the corresponding symbol. Columns (a) and (b) show the basis orbital energies of II before and after intramolecular through space and/or through bond interaction. Columns (g) and (f) have the same significance than (a) and (b), but correspond to IV(H).

6) In contrast to II, the orbital energies in III and IV(H) are no longer split symmetrically with respect to those of the interacting pairs of basis orbitals. This was to be expected. Increasing tightness of the cage molecule will induce increased mixing with other σ-orbitals, and as a consequence the simple approximation used in the above discussion becomes less valid. This is also shown by the Extended Hückel calculations.

Concluding Remarks

The P.E.-spectrum of IV(CH_3) shows that dimethyl substitution leads to the following positive shifts in the orbital energies of the four highest occupied orbitals of IV(H): $\varepsilon(a'(\underline{\pi}-\Delta)) = -8.3$ (shift +0.2), $\varepsilon(a''(\underline{\pi}-\Delta)) = -8.7$ (shift +0.1), $\varepsilon(a''(\underline{\Delta}+\pi)) = -10.0$ (shift +0.4), $\varepsilon(a'(\underline{\Delta}+\pi)) = -11.1$ (shift +0.4), all values in eV. In agreement with our assignment the two orbitals $a''(\underline{\Delta}+\pi)$ and $a'(\underline{\Delta}+\pi)$ with higher Walsh-character are shifted more than the two highest occupied orbitals $a'(\underline{\pi}-\Delta)$ and $a''(\underline{\pi}-\Delta)$. The obvious reason is, that one of the methyl-groups in IV(CH_3) is directly attached to the three-membered ring.

In conclusion we believe that the results obtained for III, IV(H), IV(CH_3), V and VI constitute good evidence in favour of the orbital assignment proposed for II and I.

This work is part of project No. SR 2.120.69 of the Schweizerischer Nationalfonds. We wish to thank CIBA-GEIGY S.A. for financial support and SANDOZ S.A. for the gift of computer time.

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