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CONJUGATIVE INTERACTION BETWEEN CYCLOPROPYL WALSH ORBITALS AND π-ORBITALS IN DISPIRO[2.2.2.2]DECA-4,9-DIENE[1]

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Photoelectron (PE) spectroscopic evidence has shown unequivocally that the Walsh orbitals of a cyclopropyl group and the π orbitals of a neighboring double bond interact strongly when the vinylcyclopropane system is in a synperiplanar or antiperiplanar conformation[2,3]. It was of interest to compare the degree and type of this interaction in dispiro[2.2.2.2]deca-4,9-diene (1)[4] with that in spiro[2.4]hepta-4,6-diene[2b] and dispiro[2.0.2.4]deca-7,9-diene[3]. We here report our preliminary interpretation of the PE spectrum of (1).

(1)

(2)

(3)

(4)

Our assignment of the first four bands in the experimental spectrum of (1)[5a] (see Table 1) is based on the PE data for the reference compounds 3,3,6,6-tetramethylcyclohexa-1,4-diene (2) and dispiro[2.2.2.2]decane (3)[5b] and on MINDO/2 calculations[7]. Assuming the validity of Koopmans' theorem[8] the bands I_1 = 8.81 and I_2 = 9.32 eV in the spectrum of (2) have to be assigned to the π MO's, the lower ionization potential (IP) probably corresponding to the symmetric combination ($\pi_1 + \pi_2$) (see Fig.1)[9]. Compared to cyclohexa-1,4-diene the π levels of (2) are inductively destabilized by the methyl groups by ≈ 0.5 eV and the split between the two is only 0.51 eV because of a smaller through-bond interaction. This is in agreement with the results of MINDO/2 calculations which predict the same energy for the highest filled π MO of (2) and cyclohexa-1,4-diene as well as a 0.5 eV smaller split between the π levels of (2).

(3) has a chair conformation[10] and therefore C_{2h} symmetry. The combinations ($e_{A1} - e_{A2}$)

and $(e_{S1} + e_{S2})$ of the cyclopropyl Walsh orbitals have a_g, the other two combinations $(e_{A1} + e_{A2})$ and $(e_{S1} - e_{S2})$ have b_u symmetry, they can be assigned to the bands $I_1 = 9.17$ eV (a_g), $I_2 = 9.91$ eV (b_u), $I_3 = 10.18$ eV (a_g) and $I_4 = 10.58$ eV (b_u). From MINDO/2 results (Fig.2) we expect all Walsh orbitals of the hypothetical planar dispirodecane (4) to be slightly destabilized with respect to the chair conformation (3), and the b_{2g} and a_{1g} orbitals to be nearly degenerate; this leads to the estimated ionization potentials for planar (4): $I_1(b_{2g}) \approx 9.6$ eV, $I_2(a_{1g}) \approx 9.8$ eV, $I_3(b_{1u}) \approx 10.0$ eV and $I_4(b_{3u}) \approx 10.4$ eV.

TABLE 1. Vertical Ionization Potentials I_n in eV for Compounds (1) - (3) and assignment to MO's ψ_n.

(1)		(2)		(3)	
I_n	ψ_n	I_n	ψ_n	I_n	ψ_n
7.82	b_{1u}	8.81	b_{1u}	9.17	a_g
9.44	b_{3g}	9.32	b_{3g}	9.91(s)	b_u
10.29	a_{1g}	10.25	σ	10.18	a_g
10.93	b_{3u}	11.10		10.58	b_u
12.61		11.94		11.61	
12.94		13.49		11.92	

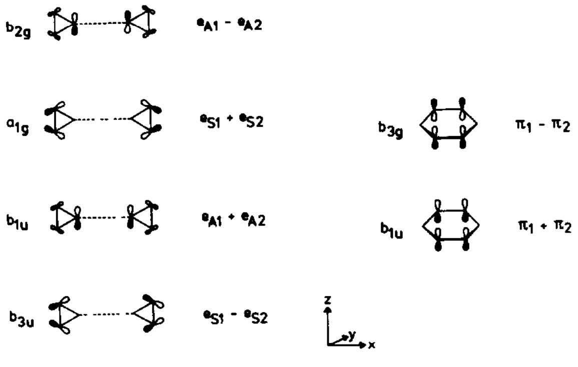

FIGURE 1: Classification of Walsh- and π-MO's According to D_{2h} Symmetry

On the basis of the above assignment for (2) and the estimated data for (4) the spectrum of (1)[11] can be interpreted reasonably well: The energies of the a_{1g} and b_{3u} orbitals should change little upon the transition from (4) to (1), b_{3g} should have about the same energy as in (2) and as a pure π-MO should differ from the others in its band shape. The b_{1u} orbital should be destabilized strongly because of the interaction between the $(e_{A1} + e_{A2})$ and the $(\pi_1 + \pi_2)$ combination, whereas the b_{2g} orbital is expected to be stabilized by interaction with the LUMO $(\pi_1^* + \pi_2^*)$. This leads to the assignment given in Table 1, with differs from the one which would be obtained by mere comparison of experimental IP's with computed MO energies insofar as the order of the b_{3g} π orbital and the a_{1g} and b_{3u} Walsh orbitals is interchanged. This interchange seems plausible because the latter MO's have the same symmetry as σ MO's for which the MINDO/2 approach tends to give too high orbital energies[2c]. Irrespective of which assignment is assumed the splitting of the b_{1g} orbitals can be estimated from the first IP and the mean value of the basis energies (b_{1g} in (2) and in (4) without through-bond interaction)to be approximately 4.1 eV, leading to $\beta = -1.8$ eV for the interaction between π and Walsh orbitals, in fair agreement with the value $\beta = -1.9$ eV[2b] and $\beta = -2.15$ eV[2c] obtained previously.

The interpretation of the PE spectral data of (1), (2) and (3) leads to the conclusion, that spirocyclopropyl groups as in (1) can transmit the electronic effect between the two π-bonds in a cyclohexa-1,4-diene far better than C-C-σ-bonds as in (2) and the C-H-σ-bonds as in cyclohexa-1,4-diene itself.

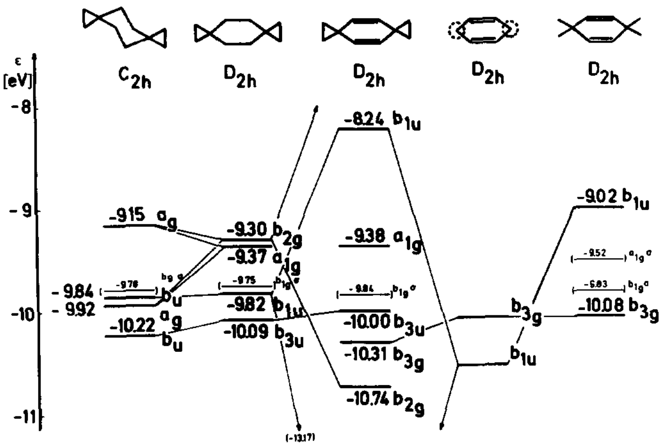

FIGURE 2: Correlation of MINDO/2 π and Walsh orbital energies for dispirodecane (3), planar dispirodecane (4), dispirodecadiene (1), cyclohexa-1,4-diene without through-bond interaction and tetramethyl-cyclohexa-1,4-diene (2).

REFERENCES AND FOOTNOTES

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[5]a) A modification of the published procedure[4] was used for the preparation of (1): 2,5-dimethylenecyclohexane-1,4-diol was silylated with trimethylsilyl chloride/pyridine, the resulting bistrimethylsilyl ether upon cyclopropanation using the Conia modification[6] of the Simmons-Smith reaction and subsequent methanolysis gave dispiro[2.2.2.2]decane-4,9-diol in 75% overall yield. b) (3) was obtained by the Wolff-Kishner reduction of a sample of dispiro[2.2.2.2]decan-4,9-dione[4].

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[11] (1) can be assumed to be almost planar, since cyclohexa-1,4-diene deviates from planarity only slightly. Cf.l.c. [10], [9].