171. π-Orbital Interactions in *Möbius*-Type Molecules as Studied by Photoelectron Spectroscopy

by **Edwin Haselbach** and **Louis Neuhaus**
Institut de chimie physique, Université de Fribourg, CH-1700 Fribourg
Richard P. Johnson
Department of Chemistry, Iowa State University, Ames, Iowa 50011, U.S.A.
Kendall N. Houk
Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, U.S.A.
and **Michael N. Paddon-Row**
Department of Chemistry, New South Wales Institute of Technology, Australia

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Summary

Some benzobarrelenes were studied by photoelectron (PE.) spectroscopy. The results can be interpreted by considering dominant through-space interaction of the π-molecular fragments in a *Möbius*-fashion. Some chemical features of the substrates are rationalized on the basis of these findings.

Introduction. – Barrelene (**1**), first synthesized by *Zimmerman & Paufler* in 1960 [1], clearly may be considered the archetypal *Möbius* molecule. Homoconjugative interaction among the three π-bonds must, by symmetry, involve an odd number of negative (antibonding) overlaps, regardless of how the π- and π*-basis orbitals are defined in space. Detailed treatments of barrelene molecular orbitals have been presented elsewhere; the resulting orbital sequence [1] [2] is given in *Figure 1*. For a through-space interaction of magnitude β, a pair of degenerate antibonding and bonding MO's is lowered by β, with respect to the basis, while

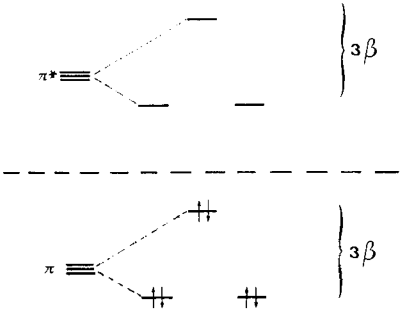

Fig. 1. *π-Molecular orbitals of barrelene derived from three interacting ethylene fragments*

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the remaining two orbitals are raised by 2β. The overall splitting ($\Delta\varepsilon$) is 3β in the bonding and antibonding manifold.

In a previous study [3] we have shown by PE. spectroscopy that this simple MO-treatment of barrelene is indeed quite valid, with two exceptions. First, there is apparently a significant contribution from hyperconjugative interaction with the lower-lying σ-skeleton for some π-levels, with the top one (the HOMO) excluded. This proved difficult to assess quantitatively, but is supported by recent MO-calculations by *Meyer & Pasternak* [4]. Second, there is a *Jahn-Teller* distortion in the first excited state of the radical cation $\mathbf{1}^+$ which leads to a splitting of *ca.* 0.3 eV in the second ionization band.

In this communication, we continue our study of *Möbius* molecules within the usual framework of *Koopman*'s theorem and analyze the PE. spectra of a number of compounds in which one or more of the ethylenic π-orbitals have been replaced by a benzene ring [4]. These compounds include the well-known benzobarrelene (**2**), dibenzobarrelene (**3**), triptycene (**4**) series, in addition to appropriate model compounds (**5**-**9**).

We show here that orbital interactions in **2**-**4** can be understood by considering dominant through-space interaction of π-molecular fragments in a *Möbius*-fashion.


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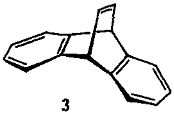
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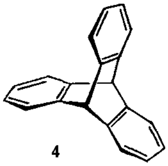
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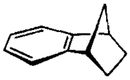
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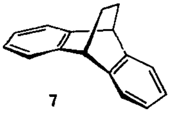
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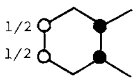
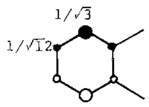
9

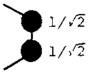
Basis molecular orbitals. - Our approach to the analysis of orbital interactions in benzobarrelenes first considers an appropriate collection of basis molecular orbitals [5]. We can then semi-quantitatively assess the relative through-space and through-bond contributions in model compounds **6**, **7** and **8** and extend these to the fully homoconjugated systems **2**, **3** and **4**. Our initial collection of basis orbitals is simply the two highest-occupied benzene MO's, Ph_S and Ph_A and a bonding π-MO, π_S. The energies of these are taken as those of **5** [5] and **9**[3] ($Ph_S = -8.45$ eV; $Ph_A = -8.95$ eV; $\pi_S = -9.05$ eV).



Ph_S



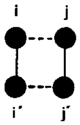
Ph_A



π_S

Neglecting overlap, through-space interactions of these orbitals can be calculated by first-order perturbation theory or, alternatively, by simple HMO-calculation. In the general case for homoconjugative interaction of two π-MO's, the resulting orbital splitting is given by *Equation 1.*

$$\Delta\varepsilon = 2\beta = 2(C_iC_j + C_i'C_j')\beta^0. \qquad (1)$$



Here C_i/C_j and C_i'/C_j' are the orbital coefficients at the sites of nearest neighbor nonbonded interaction, β^0 is the resonance integral between the two basis atom (nonbonded) p-orbitals and $\Delta\varepsilon$ is the splitting of the two resulting π-orbitals. For the different possible types of basis-orbital interactions, we calculate the following $\Delta\varepsilon$-values *(Eqn. 2–5).*

$$\pi_S^1/\pi_S^2 \quad \Delta\varepsilon = 2\beta \qquad (2)$$

$$Ph_S^1/Ph_S^2 \quad \Delta\varepsilon = \beta \qquad (3)$$

$$Ph_A^1/Ph_A^2 \quad \Delta\varepsilon = 1/3\beta \qquad (4)$$

$$Ph_S/\pi_S \quad \Delta\varepsilon = 2/\sqrt{2}\beta \qquad (5)$$

For the Ph_S/π_S-interaction, we here assume degeneracy; in practice, this interaction will decrease as the energy difference between Ph_S and π_S increases.

We next consider the symmetrical fully homoconjugated MO's in barrelene (**1**) and triptycene (**4**). Here, each basis π-orbital interacts twice with other orbitals. This leads us to the following results for the orbitals of interest, with interactions being uniquely determined by symmetry *(Eqn. 6–8).*

$$\pi_S^1/\pi_S^2/\pi_S^3 \quad \Delta\varepsilon = 3\beta \text{ for } \mathbf{1} \qquad (6)$$

$$\left.\begin{array}{ll} Ph_S^1/Ph_S^2/Ph_S^3 & \Delta\varepsilon = 3/2\beta \quad (7) \\ Ph_A^1/Ph_A^2/Ph_A^3 & \Delta\varepsilon = 1/2\beta \quad (8) \end{array}\right\} \text{for } \mathbf{4}$$

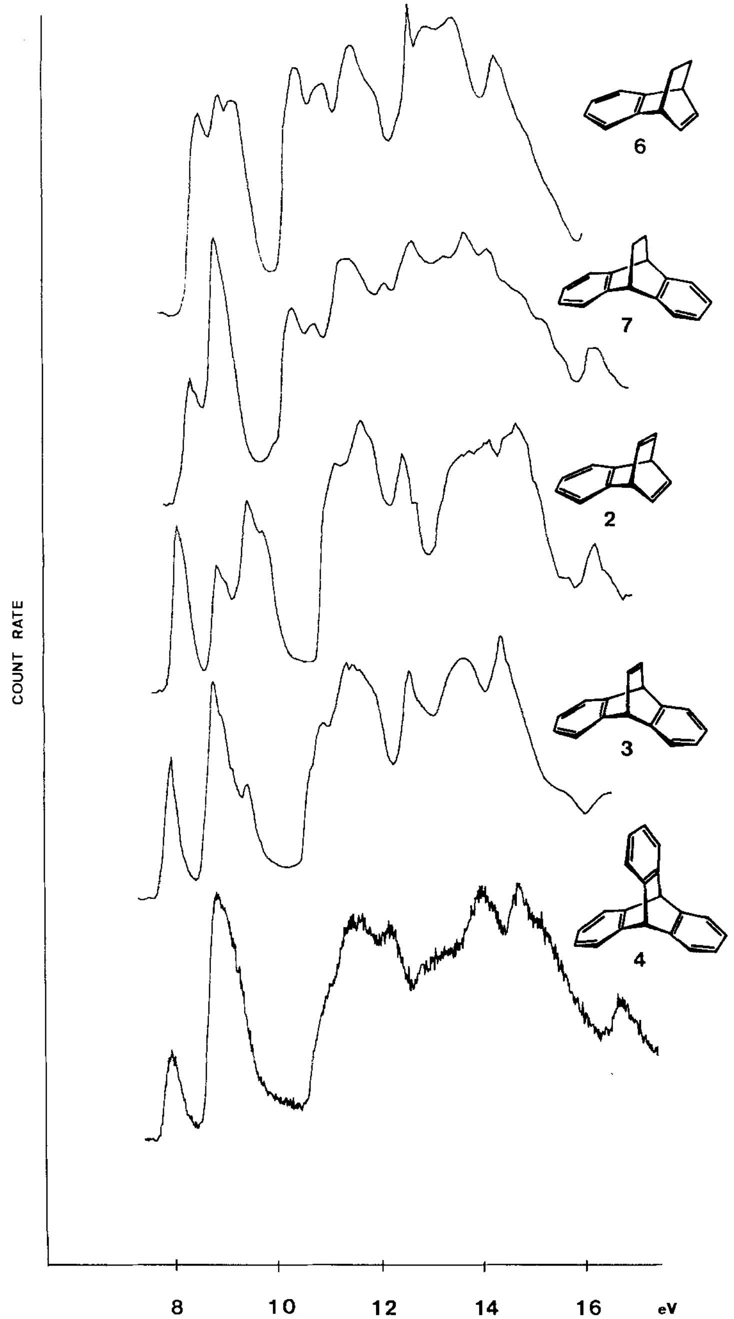


Fig. 2. *He(I)-PE. spectra of compounds* **2**, **3**, **4**, **6** *and* **7** (Due to different scales in the original spectra collected at different laboratories, they were redrawn using an *Apple Graphics Tablet*, the uniform scale being set by the spectrum of **4**. As a result, the upper four spectra are smoothed with respect to noise and/or vibrational fine structure)

A critical feature in this type of analysis is the chosen value of the interaction parameter β; in practice this usually is determined empirically. Furthermore, we need to distinguish between fully and partly homoconjugated systems. The former case is best represented by barrelene (**1**) itself with $\beta \approx -0.54$ eV, while β for the latter is taken as -0.29 eV. These values are easily derived from the experimentally observed orbital splittings in barrelene (**1**) (1.61 eV $= -3\beta$) [3] and dihydrobarrelene (**8**) (0.58 eV $= -2\beta$) [6]. The difference between these two values has been ascribed largely to differences in geometry [6].

Our analysis does not entirely ignore through-bond (hyperconjugative) effects since these are included to a certain degree in the empirically determined β-values. Furthermore, corrections for inductive effects based on appropriate model compounds will be made.

Results. - He(I)-PE. spectra were measured for the compounds **2**, **3**, **4**, **6** and **7**, preparations of which are described in [7]. The spectra are reproduced in *Figure 2* and the results summarized in the *Table*, together with the literature values for **1**, **5**, **8** and **9**.

Table. *Relevant vertical ionization potentials* (eV) *for barrelene derivatives measured by PE. spectroscopy*

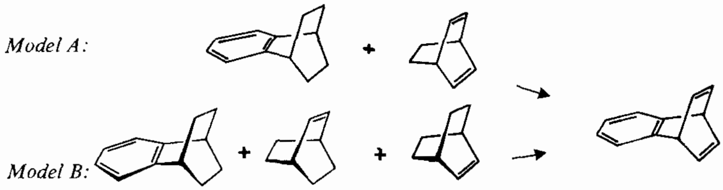
Compound	Vertical ionization potentials [eV]
1	8.23, 9.65[a]), 10.02[a]) [3]
2	8.12, 8.84, 9.45, 9.75, 11.5
3	8.0, 8.78[b]), 9.50
4	7.9, 8.9[b])
5	8.45, 8.95 [5]
6	8.54, 8.94, 9.20
7	8.30, 8.80[b]), 10.3
8	8.87, 9.45 [6]
9	9.05 [6]

[a]) *Jahn-Teller* components. [b]) Broad band from overlap of several ionizations.

Discussion. - We consider first the PE. spectra of model compounds **6** and **7**, which involve only one homoconjugative interaction. For **6**, Ph_A should be essentially unchanged relative to model compound **5** (-8.95 eV), while through-space interaction of Ph_S and π_S will be small (*ca.* 0.1-0.15 eV) since these are strongly nondegenerate from a comparison of **5** and **9**. This is essentially what is observed. We assign the three ionizations at 8.54, 8.94 and 9.20 eV as corresponding to the levels ($Ph_S - \pi_S$), Ph_A and ($\pi_S + Ph_S$), respectively. In this case, the lowering of π_S is primarily of inductive origin. Ph_S will be raised through-space and lowered inductively, with little net change.

For **7**, we anticipate interaction between degenerate pairs of phenyl orbitals. From *Equation 3* and assuming $\beta = -0.29$ eV, we predict the ($Ph^1_S - Ph^2_S$) level to correspond to the ionization at 8.30 eV, in remarkably good agreement with experiment. The remaining three ionizations are predicted to occur at 8.60 ($Ph^1_S + Ph^2_S$), 8.9 ($Ph^1_A - Ph^2_A$) and 9.00 eV ($Ph^1_A + Ph^2_A$). In the observed spectrum, these are unresolved as a broad overlapping band.

We now proceed to the analysis for the fully homoconjugated mono-, di- and tribenzobarrelenes **2**, **3** and **4**. For **2** we note two possible modes of analysis. First *(Model A)* we consider the interaction of basis orbitals of benzene (Ph_A and Ph_S) with those of **8**: $(\pi_S^1 + \pi_S^1)$ and $(\pi_S^1 - \pi_S^2)$. This will emphasize interaction between the originally degenerate π-orbitals. The second model *(Model B)* considers three unmixed basis orbitals with preservation of the *Möbius* character of the orbital array.



The first possibility is shown in the interaction diagram *(Fig. 3)*. Here $(\pi_S^1 + \pi_S^2)$ and Ph_A remain essentially unchanged due to their unique symmetries. Ph_S and $(\pi_S^1 - \pi_S^2)$ are of appropriate symmetry for interaction. From simple perturbation theory, we predict $\beta = -0.54$ eV, assuming degeneracy. Experimentally, Ph_S is raised *ca.* 0.41 eV and $(\pi_S^1 - \pi_S^2)$ lowered *ca.* 0.38 eV, in good agreement with this β-value whose absolute value is an upper bound for these splits due to actual non-degeneracy of the interacting orbitals.

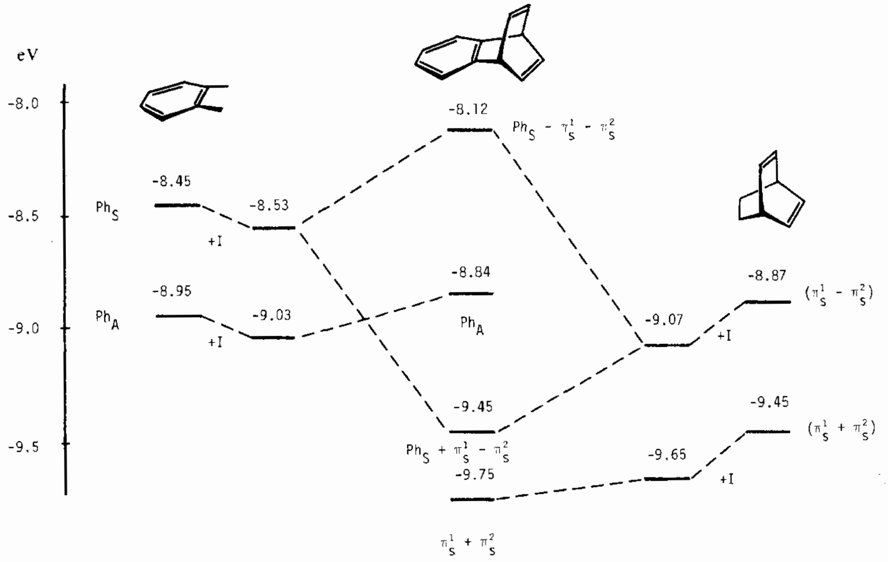


Fig. 3. *Orbital-interaction diagram for benzobarrelene*

The alternative approach is to consider the three basis orbitals Ph_S, π_S^1 and π_S^2 prior to any interaction and mix these in a fashion which preserves the *Möbius* character of the array, according to the *secular determinant 9* (in eV). Off-diagonal elements here are $\beta = -0.54$ eV from **1** (*i.e.* π_S^1/π_S^2) and $\beta = -0.38$ from *Equation 5* (*i.e.* Ph_S/π_S). Diagonalization yields the solutions $\varepsilon = -9.79$, -9.14 and -8.02 eV.

	π_S^1	π_S^2	Ph_S
π_S^1	$-9.25-\varepsilon$	$+0.54$	-0.38
π_S^2	$+0.54$	$-9.25-\varepsilon$	-0.38
Ph_S	-0.38	-0.38	$-8.53-\varepsilon$

(9)

Model A seems to better reproduce experimental results, while *Model B* is heuristically more satisfying, since it considers the full molecular symmetry.

In like manner, *Möbius* interaction in **3** can be described as in the *secular determinant 10.* Diagonalization yields the solutions $\varepsilon = -9.48$, -8.72 and -7.95 eV. The observed spectrum displays well-resolved bands at 8.00 and 9.50 eV, almost exactly as predicted, and a broad unresolved system (maximum *ca.* 8.8 eV) which corresponds to the ($Ph_S^1 + Ph_S^2$)-level (which cannot by symmetry interact with π_S) and the two Ph_A-combinations (predicted at -8.90 and -9.00 eV).

	Ph_S^1	Ph_S^2	π_S
Ph_S^1	$-8.45-\varepsilon$	$+0.27$	-0.38
Ph_S^2	$+0.27$	$-8.45-\varepsilon$	-0.38
π_S	-0.38	-0.38	$-9.25-\varepsilon$

(10)

Similar results are obtained through consideration of the alternative model; *i.e.* interaction of molecular orbitals of **7** and **9**.

Finally, we consider triptycene (**4**) which possesses six separate *Möbius* arrays derived from symmetry combinations of the six degenerate sets of bonding and antibonding orbitals of the three benzene rings *(Fig. 4).* For the Ph_S-orbitals, assuming *Equation 7* to be valid, we predict the ($Ph_S^1 - Ph_S^2 - Ph_S^3$)-combination to be at -7.91 eV (*i.e.* $-8.45 + 0.54$ eV), in excellent agreement with the experimental value (-7.90 eV). The remaining two Ph_S- and the Ph_A-combinations (with presumed *Jahn-Teller* splittings) all are observed as a broad unresolved band at *ca.* 8.9 eV, in agreement with *Figure 4.* Thus, our model correctly predicts the energy of the highest-occupied molecular orbital in triptycene with surprising accuracy. Our results thus demonstrate that through-space π/π-interaction is indeed quite significant in **4** with a magnitude essentially the same as in the parent compound **1**. Unfortunately little additional information can be derived from the complex spectrum of **4**.

Chemical consequences of orbital interactions. We consider here briefly some chemical properties of benzobarrelenes which might be influenced by interaction of π-component orbitals.

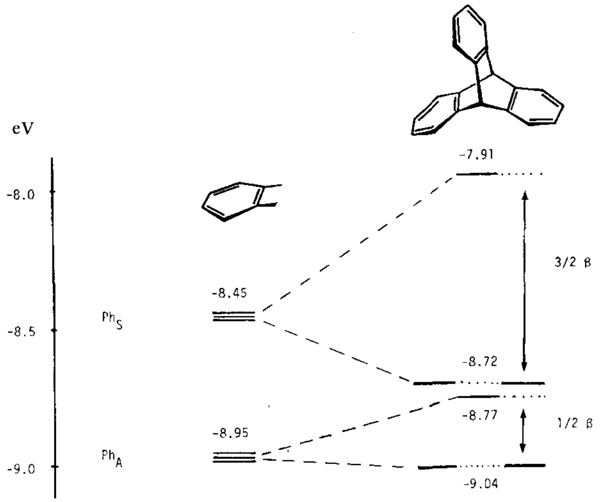


Fig. 4. *Orbital interaction diagram for triptycene, neglecting* Jahn-Teller *effects*

Concerning ground state properties, **1** exhibits an exceptionally large heat of hydrogenation for the first double bond which has recently been shown conclusively to result from through-space π/π-repulsions [8]. Our analysis indicates that **4** ought to behave qualitatively the same as **1**, which agrees with the nonclassical strain deduced from its heat of formation [9].

Isolated double bonds (*e.g.* in **9**) fail to undergo reduction in metal/ammonia solutions [10]. If H_2O is used as protonating agent for the intermediate anion, then also benzene fails to be reduced. Nevertheless, **2**, **3** and **4** are easily reduced under these conditions, the former two being attacked at their double bonds [10] [11]. Clearly, this reactivity is related to homoconjugative interaction among the virtual orbitals of the π-fragments which does follow from the present findings in the bonding manifold. The resulting low-lying acceptor orbitals provide for stabilization in the intermediate anions.

Another well-studied area is photochemical reactions. Compounds **1** [12], **2** [13], **3** [14] and **4** [15] are all well-known to undergo photoreactions involving π/π-interaction and subsequent bond formation. While we do not expect a quantitative correlation of interaction with reactivity, it is nevertheless reasonable to suppose that these factors are related. Our results also help to explain the preference of benzobarrelene (**2**) for benzo-vinyl rather than vinyl-vinyl singlet excited state bridging. HOMO → LUMO excitation in benzobarrelene should involve the transition given in *Equation 13.*

$$\mathrm{Ph_S} - \pi_{\mathrm{S}}^{1} - \pi_{\mathrm{S}}^{2} \rightarrow \mathrm{Ph_A^*} + \pi_{\mathrm{A}}^{1*} - \pi_{\mathrm{A}}^{2*} \qquad (13)$$

This transition promotes an electron from an orbital which is both benzo-vinyl and vinyl-vinyl antibonding to one which is benzo-vinyl bonding and vinyl-vinyl antibonding. Assuming this configuration to be dominant in the excited state wave function benzo-vinyl bonding should be the preferred mode of reaction, as was indeed confirmed by deuterium labeling [13]. We note in this context that such through-space orbital interactions were suggested in explaining the UV. spectra of heterocyclic analogs of benzobarrelenes [16].

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