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Dominance of Through-Bond Interaction in a *syn*-Tricyclo[6.4.0.0^{2,7}]dodecatetraene Moiety

*Rolf Gleiter**[a], *Horst Zimmermann*[a], *Wolf-Dieter Fessner*[b], and *Horst Prinzbach*[b]

Institut für Organische Chemie der Universität Heidelberg[a], Im Neuenheimer Feld 270, D-6900 Heidelberg, and

Chemisches Laboratorium der Universität Freiburg[b], Albertstr. 21, D-7800 Freiburg i. Br.

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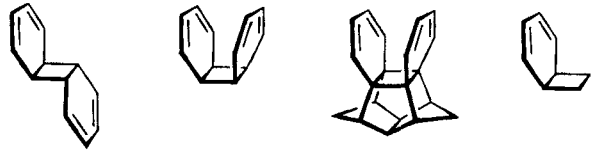
Dominanz der Through-Bond-Wechselwirkung bei einer Verbindung mit *syn*-Tricyclo[6.4.0.0^{2,7}]dodecatetraen-Einheit

Das He(I)-Photoelektronen(PE)-Spektrum von **3**, einer Verbindung mit der *syn*-Tricyclo[6.4.0.0^{2,7}]dodecatetraen-Einheit **2**, wurde durch Vergleich mit dem des *anti*-Tricyclo[6.4.0.0^{2,7}]dodecatetraens **1** und durch semiempirische Rechnungen zugeordnet. Es wird gezeigt, daß bei **3** die through-bond-Wechselwirkung zwischen den beiden Butadien-Einheiten über die through-space-Wechselwirkung dominiert.

Recently it was shown by means of He(I) photoelectron (PE) spectroscopy that in *anti*-tricyclo[6.4.0.0^{2,7}]dodecatetraene **1** ("*anti-o,o'*-dibenzene") both butadiene fragments interact strongly with each other via a through-bond mechanism[1], mediated by the relatively high lying Walsh orbitals of the four-membered ring[2]. In contrast, the two butadiene units in the *syn*-isomer **2** might interact with each other via a through-space or/and a through-bond mechanism. Compound **2** is still unknown. The polycycle **3**, however, became available via a benzene/benzene photocycloaddition[3,4], this "*syn-o,o'*-dibenzene" being surprisingly stable: $t_{1/2}$ (120°C) = ca. 130 min (benzene). The specific geometrical properties of **3**, held responsible for the long wave length UV absorption, were exploited in a crucial step (domino Diels-Alder addition) in the recently described synthesis of "pagodane", a D_{2h} $C_{20}H_{20}$-polyquinane[5]. An *X*-ray structural analysis of **3**[6] provides supportive data for the PE analysis, which is presented in this communication.



1 **2** **3** **4**

In Figure 1 the PE spectrum of **3** is shown, the recorded first vertical ionization energies ($I_{v,j}$) are collected in Table 1.

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Three bands are clearly separated from strongly overlapping bands starting at 9.8 eV. Bands ① and ③ show a typical Gaussian shape while band ② exhibits a relatively steep onset on the low energy side and vibrational fine structure.

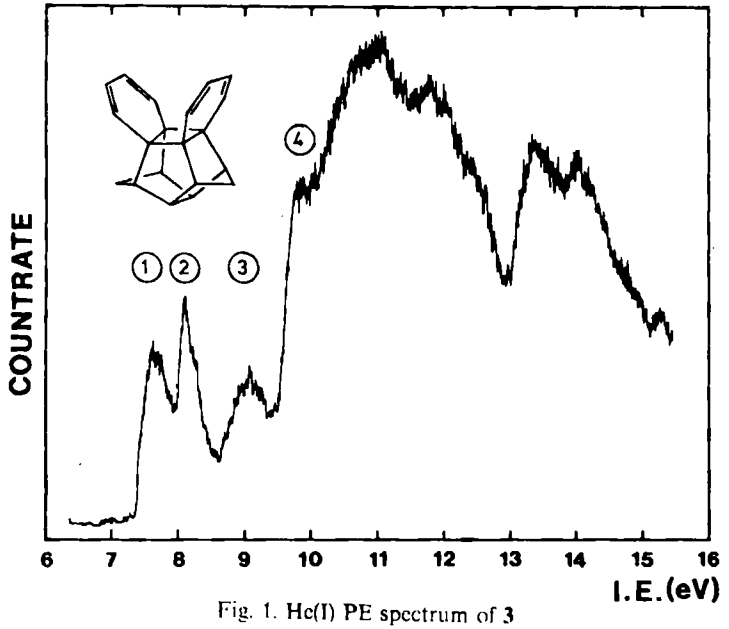

Fig. 1. Hc(I) PE spectrum of **3**

Table 1. Comparison between the measured vertical ionization energies, $I_{v,j}$, and the calculated orbital energies of **3**. All values in eV

Band	$I_{v,j}$	Assignment	$-\varepsilon$(MINDO/3)	$-\varepsilon$(ZDO)
①	7.6	b_1 (π_+)	7.93	7.55
②	8.1	a_2 (π_-)	8.76	8.05
③	9.1	b_2 (W)	8.97	9.10
④	9.65	σ	9.47	

To interprete the PE spectrum of **3** we make use of Koopmans' theorem[7]. In this approximation the measured vertical ionization energy, $I_{v,j}$, is set equal to the calculated orbital energy ε_j ($I_{v,j} = -\varepsilon_j$). This approach allows to correlate orbital energies and PE bands and seems to be valid for the outer valence orbitals of most organic molecules. The analysis rests on the comparison of the PE spectrum of **3** with those of related compounds (**1**/**4**) and of the calculated orbital energies/molecular orbitals (MINDO/3[8,9]) with the ionization energies.

Empirical Assignment

To estimate the ionization energy for the antisymmetric π-combination of the butadiene fragments in **3** we briefly consider the PE spectrum of **4**[1]. It shows one band at 8.25 eV well separated from the rest of the spectrum. It has been assigned to the highest occupied π-orbital of the butadiene fragment. From this we conclude that the first two bands in the

spectrum of **3** are due to ionizations from the two symmetry-adapted linear combinations involving the HOMO of butadiene, $b_1(\pi_+)$ and $a_2(\pi_-)$. The sequence of both MO's depends on the magnitude of the through-space and the through-bond interaction. To estimate this from the PE spectrum we consider the possible interaction patterns for **3** in Figure 2. On the left-hand side of this Figure the two linear combinations of the π MO's a_2 and b_2 are shown. The spatial interaction of both will stabilize $b_1(\pi_+)$ and destabilize $a_2(\pi_-)$. The π_+ linear combination is also suited for a considerable interaction with the corresponding Walsh orbital of the four-membered ring, while π_- has no such partner. The corresponding interaction pattern is shown at the right of Figure 2.

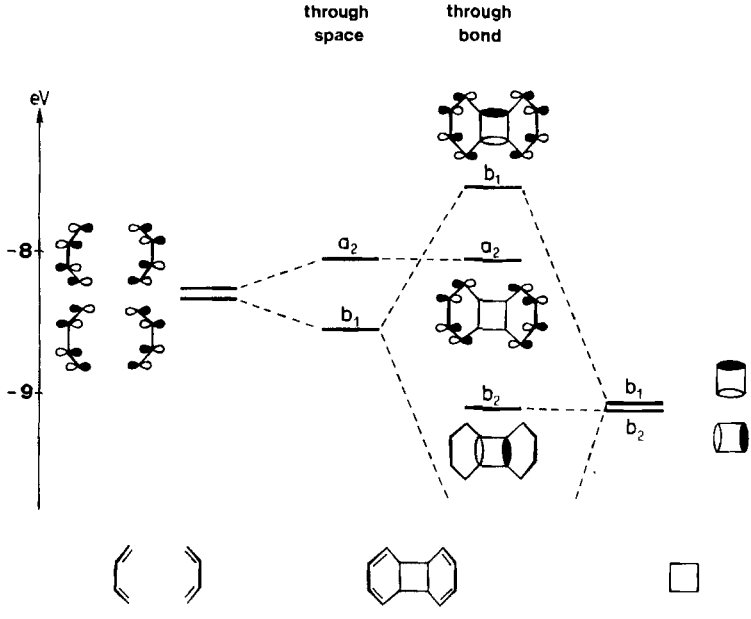

Fig. 2. Interaction diagram between two butadiene moieties through space and through bond via a cyclobutane ring

To decide whether the patterns shown in Figure 2 correspond to the band sequence of **3** we consider the band shapes. The Gaussian shape of bands ① and ③ indicates a different geometry between ground and ionic states. Such a shape is usually encountered when a strong σ-participation is found in the MO's the electron is ejected from. A steep onset is typical for weakly bound π MO's with small or no σ-participation. These arguments clearly favour $b_1(\pi_+)$ on top of $a_2(\pi_-)$ followed by the b_2 Walsh orbital.

Calculations

To aid our assignment we have carried out semiempirical calculations on **3** (results in Table 1). The geometrical parameters adopted for our calculations were those obtained from the *X*-ray analysis[6]. The calculated orbital energies agree reasonably well with the measured ones and confirm our assignment discussed for the first three bands. The given assignment (Table) is further supported by the correlation between the first PE bands of **1** and **3** shown in Figure 3.

Due to the alkyl substitution of the cyclobutane fragment in **3** we anticipate a stronger shift for the cyclobutane Walsh orbitals compared to the π MO's. This is indeed found as shown in Figure 3.

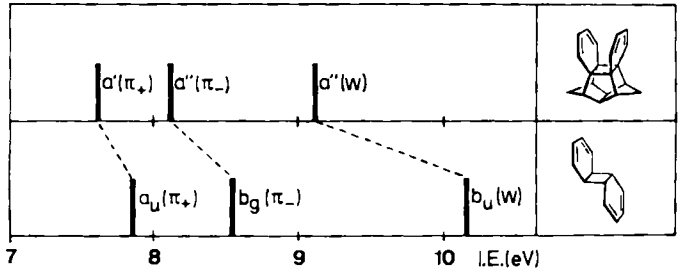

Fig. 3. Correlation between the first PE bands of **1** and **3**

Concluding Remarks

To judge roughly the magnitude of the through-space and through-bond interaction prevailing in **3** we have used a ZDO type calculation. To estimate the basis orbital energy of the Walsh e-orbitals of the cyclobutane fragment in **3** we use band ③ of its PE spectrum.

$$\varepsilon(b_2, W) = \varepsilon(b_1, W) = -9.1 \text{ eV}$$

For the basis orbital energy of the butadiene moieties we use $\varepsilon(\pi) = -8.3$ eV. We have raised the corresponding basis energy in **1**[1] due to the larger σ frame by 0.2 eV.

To reproduce the spectral pattern found in the PE spectrum of **3** we reach a satisfactory agreement if we assume a value of $\beta = -0.25$ to -0.30 eV for the through-space interaction (in Figure 2 and in the Table we assumed -0.25 eV). For the through-bond interaction we adopted the same values as in **1** ($\beta = -1.5$ eV)[1]. The orbital interaction diagram presented in Figure 2 and the values shown in Table 1 are based on the results just discussed. In this qualitative estimate we encounter a relatively small through-space interaction. This can be rationalized by the relatively large interatomic distances between the two butadiene fragments. The *X*-ray analysis reveals an average value of 3.06 Å between the centers 1,4 and 1',4' and 4.27 Å between centers 2,3 and 2',3' of the butadiene moieties, respectively.

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Experimental Part

The PE spectrum of **3** has been recorded with a PS 18 photoelectron spectrometer (Perkin Elmer Ltd., Beaconsfield, England). The preparation of **3** as well as the *X*-ray structural analysis are reported elsewhere[3,6].

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