Chem. Ber. **117**, 1987 – 1990 (1984)

Photoelectron Spectra of Some Reduction Products of [2.2]Paracyclophane

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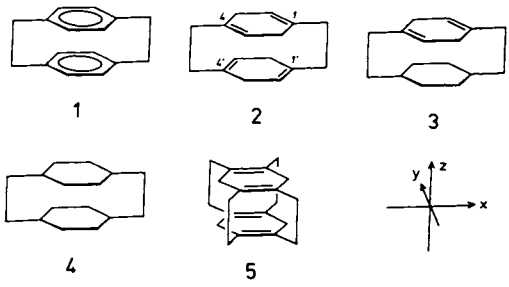
Received November 22, 1983

Photoelektronenspektren einiger Reduktionsprodukte von [2.2]Paracyclophan

Anhand des He(I)-Photoelektronen(PE)-Spektrums von 2,3',5,6'-Tetrahydro[2.2]paracyclophan (**2**) wird gezeigt, daß die Through-Bond-Wechselwirkung zwischen den Sechsringen klein, innerhalb der Cyclohexadienringe aber groß ist. Über die PE-Spektren der weiteren Hydrierungsprodukte **3** und **4** wird berichtet.

[2.2]Paracyclophane (**1**) undergoes the Birch reduction to give the tetrahydro product **2**, 2,3',5,6'-tetrahydro[2.2]paracyclophane[1-4]. The electronic structure of this chiral D_2 tetraene system has been investigated by UV and CD spectroscopy[1,2,5].



In this communication, we present the photoelectron (PE) spectrum of **2**, together with the PE spectra of the corresponding octahydro and perhydro products **3** and **4**.

The PE spectra are shown in Fig. 1 and observed and calculated ionization energies for **2** are given in Table 1. The low-energy composite PE band of **2** with maxima close to 8.3 and 8.8 eV can be assigned to ejection of electrons from the four π type molecular orbitals (MOs) associated with the ethylenic double bond. The approximate shape of these MOs is shown in Fig. 2. The results of semiempirical calculations indicate that the interaction between the four ethylenic π functions is dominated by intradeck through-bond coupling via the methylene groups of the cyclohexadiene rings[6], leading to the prediction of $11a$ (π) and $10b_1$ (π) on top of $11b_3$ (π) and $10b_2$ (π). However, this result is sensitive to the assumed molecular geometry (vide infra). The

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third band of **2** with a maximum at 10.6 eV can be assigned to the two near-degenerate σ ribbon orbitals $9b_1$ (σ) and 10a (σ). The band observed at 10.3 eV in the spectrum of **1**[7] can probably be assigned to a σ orbital corresponding to the $9b_1$ orbital of **2** (b_{1u} in D_{2h}).

In contrast to the case of **1**, it is possible to construct an essentially "strain-free" Dreiding model of **2**. However, the distance between the centers 1 and 1' (or 4 and 4') is then only ≈ 2.6 Å.

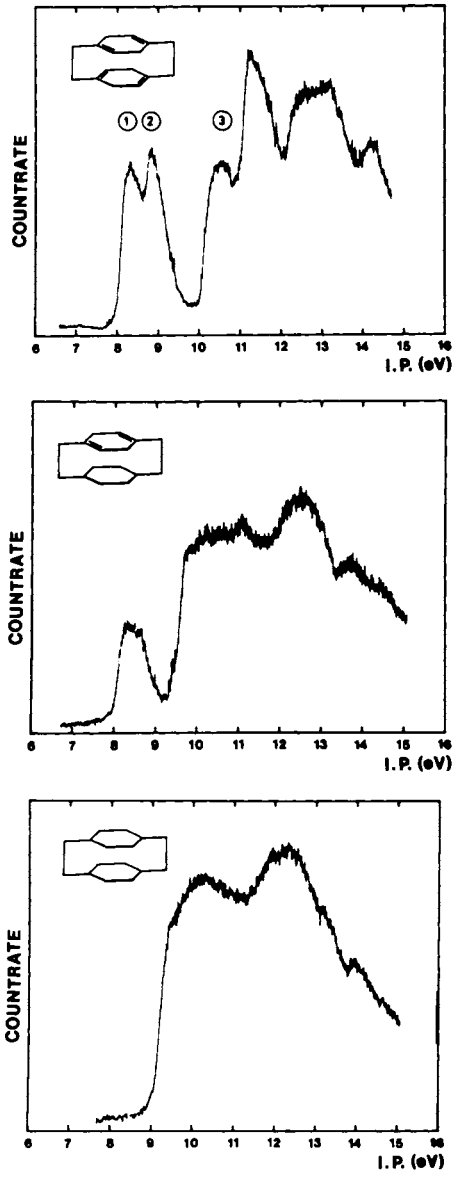

Fig. 1. He(I) PE Spectra of **2** – **4**

Table 1. Observed Photoelectron Band Maxima I_i and Calculated Orbital Energies E_j for 2,3',5,6'-Tetrahydro[2.2]paracyclophane (2) (eV)

Band	I_i	Orbital Assignment	$-E_j$ MINDO/3	$-E_j$ MNDO/1
①	8.3	11a (π)	8.89	9.37
		$10b_1$ (π)	8.95	9.40
②	8.8	$11b_3$ (π)	9.15	9.56
		$10b_2$ (π)	9.36	9.67
③	10.6	$9b_1$ (σ)	10.06	11.66
		10a (σ)	10.06	11.77

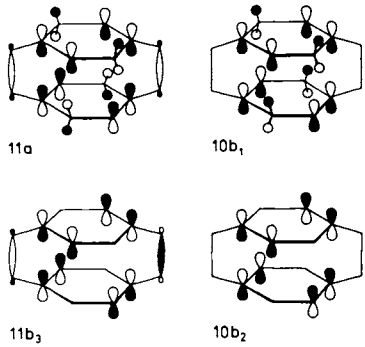

Fig. 2. Schematical Indication of the Shape of the Four Highest Occupied MOs of 2,3',5,6'-Tetrahydro[2.2]paracyclophane (2) (cf. Table 1)

It is expected that in the real molecule this distance is increased; MINDO/3[8] and MNDO/1[9] predict 3.1 and 2.9 Å, respectively. As a result, the cyclohexadiene rings are distorted from a boat to a twist-like conformation with slightly non-planar double bonds.

In order to estimate the significance of interdeck interaction, *Marshall* and *Hall*[5] performed a series of CNDO/2[10] calculations on two ethylenes situated at various distances. They found that the calculated total energy is independent of the distance in the range 2.8 – 10.0 Å and therefore concluded that interaction between the two decks in **2** contributes substantially nothing to the electronic transitions. However, the calculation of *Marshall* and *Hall* (which demonstrates only the failure of CNDO/2 to reproduce the repulsion between closed shells) is irrelevant to the discussion of the spectroscopic properties of **2** since it does not consider the energies of the excited states which depend on conjugative, exciton, and charge resonance interactions.

As expected, the interdeck through-space conjugative interaction in **2** is predicted by MINDO/3 and MNDO/1 to be very sensitive to the 1,1' and 4,4' separation; the π orbital sequence (Table 1) obtained on the basis of the optimized geometries is reversed under the assumption of a geometry corresponding to the Dreiding model (leading to $11b_3$ (π), $10b_2$ (π) > $10b_1$ (π), 11a (π)). Through-bond interaction via the ethano bridges seems relatively insignificant. A similar conclusion has been drawn from the investigations on **5** which shows four strongly overlapping bands around 8 eV[7].

The PE spectrum of **3** is featured by a broad π band with maximum close to 8.4 eV followed by the onset of compact structures around 9.7 eV. The onset of the unresolved "σ mountain"

characterizing the spectrum of **4** is observed around 9.4 eV. **3** and **4** are highly strained, internally crowded substances, probably involving a gross violation of the van der Waals radii and/or a severe distortion of bond angles[11]. In view of these difficulties, we shall refrain from further discussion of the electronic structure of these compounds at this time.

We are grateful to the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *BASF Aktiengesellschaft* in Ludwigshafen for financial support.

Experimental Part

2,3',5,6'-Tetrahydro[2.2]paracyclophane (**2**) and perhydro[2.2]paracyclophane (**4**) were obtained from [2.2]paracyclophane (**1**) according to published procedures by either subjecting **1** to the Birch reduction[1-3] or completely hydrogenating it over platinum (acetic acid, 70°C, 3 d)[11]. The hydrocarbons were purified by chromatography/recrystallization and their structures verified by spectral comparison.

1,2,2',3,4,5,5',6-Octahydro[2.2]paracyclophane (**3**): 0.10 g (0.48 mmol) of **1** in 30 ml of ethyl acetate and 15 ml of acetic acid was hydrogenated over 50 mg of platinum at room temperature. After the uptake (19 h) of 35 ml (1.56 mmol) of hydrogen the product mixture was separated by thick layer chromatography (silica gel, tetrachloromethane): **3** was isolated as a waxy solid (36.4 mg, 35%), the remainder consisting mostly out of **1**. – ^{1}H NMR ($CDCl_3$, int. TMS): δ = 5.5 (m, 2H, CH=C), 2.8 – 1.1 (several overlapping multiplets, 22H, CH and CH_2). – IR (KBr): 2986 (vw), 2960 (m), 2910 (m), 2840 (m), 1485 (w), 1465 (w), 1445 (w) und 1415 cm^{-1} (w). – MS: *m/e* = 216 (100%), 201 (36), 187 (54), 174 (36), 159 (34), 145 (39), 133 (41), 119 (57), 106 (79), 93 (92), 79 (87).

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