Quest for a Strong Through Bond Interaction in [2.2]Paracyclophane

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Received November 11, 1981

Eine starke Through-Bond-Wechselwirkung in [2.2]Paracyclophanen

Das He(I)-Photoelektronen(PE)-Spektrum von [1 : 2;9 : 10]Bismethano[2.2]paracyclophan (**2**) wurde gemessen. Der Unterschied zwischen der ersten Bande von **2** und der ersten Bande im PE-Spektrum von [2.2]Paracyclophan (**1**) wird als Hinweis dafür gewertet, daß in **2** eine noch stärkere σ,π-Wechselwirkung vorhanden ist als in **1**.

Some time ago it was pointed out that in [2.2]paracyclophane (**1**)[1] the $b_{3u}(\pi)$ orbital interacts strongly with the corresponding σ combination of the C_2H_4 bridges. To investigate this prediction in principle two different cases must be considered: either the energy of the $b_{3u}(\sigma)$ orbital is lowered and thus the $\pi - \sigma$ interaction is reduced or the $b_{3u}(\sigma)$ orbital energy is raised and the $\pi - \sigma$ interaction is increased. The first case has been studied by *Heilbronner* and *Maier*[2] who utilized the perfluoro effect in 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane. They showed by means of He(I) photoelectron(PE) spectroscopy that due to this effect the ionization from the b_{3u} orbital of **1** occurs at considerably higher energy than from the b_{2g} and b_{3g} orbitals.
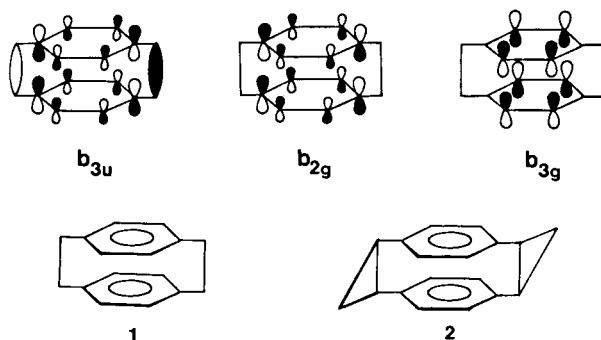
In this note we present an example for the second possibility: In the recently synthesized [1 : 2;9 : 10]bismethano[2.2]paracyclophane (**2**)[3] the basis orbital of the $C - C$ σ bond connecting the two rings is considerably higher in energy[4] and thus according to the qualitative interaction diagram shown in Fig. 1 we expect a shift of the b_{3u} level towards higher energy.
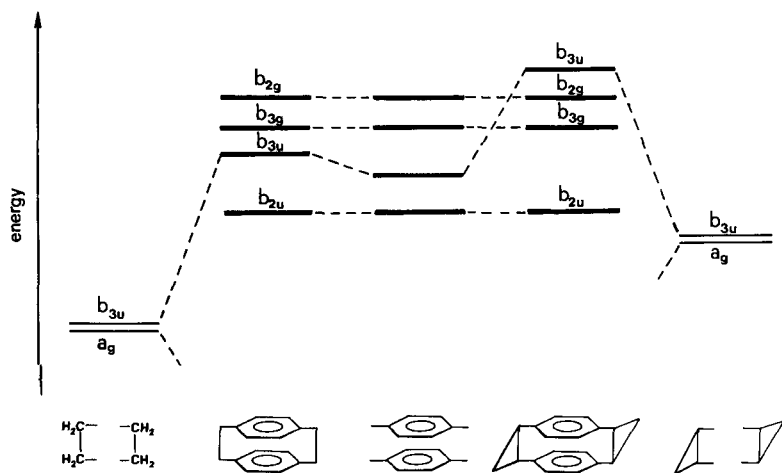
Fig. 1. Qualitative interaction diagram between the $C-C$ σ-orbitals and the π-system in **1** (left) and **2** (right)
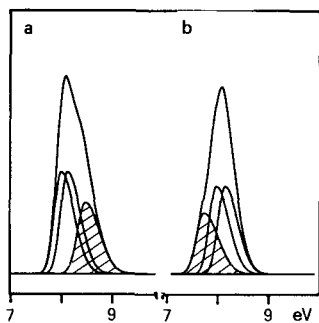

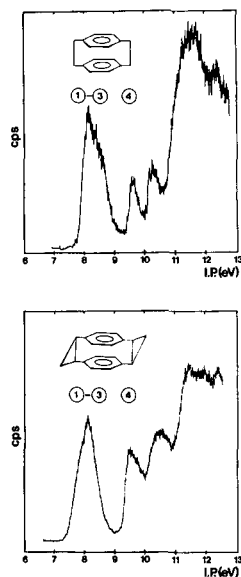Fig. 2. Tentative deconvolution of the first composite PE band of **1** and **2**

Fig. 3. Comparison between the He(I) PE spectrum of **1** and **2**

The situation shown in Fig. 1, *i. e.* the nearly constant energy of b_{2g} and b_{3g} and a large shift of b_{3u} may give rise to only small changes in the resulting band. To exemplify this situation we have constructed one broad band by superposition of three bands (Fig. 2), two with half widths typical for ionizations from π-orbitals and one with a larger half width typical for π-bands with σ participation. Although the center of the latter band has been shifted by about 1 eV, the shape of the resulting composite band has not changed very much. A comparison with the first band in the PE

spectra of **1** and **2** shows that the band in Fig. 2a is very similar to the first band in the PE spectrum of **1** (Fig. 3) and the band in Fig. 2b simulates very well the first band in the PE spectrum of **2** in Fig. 3.

We interpret the difference in the first bands in the PE spectra of **1** and **2** as due to the shift of the "$^2B_{3u}$" state[5] of **2**$^+$ towards lower energy compared with the states ("$^2B_{2g}$" and "$^2B_{3g}$") responsible for the other two components of the first peak. This assignment is based on Koopmans' approximation ($- \varepsilon_j = I_{v,j}$)[6] using molecular orbital calculations of the MINDO/3[7] type. These calculations predict a small shift from **1** to **2** for the highest molecular π-orbitals as anticipated from the larger σ-frame in **2**, but a large shift due to a strong through bond coupling[8] for the b_{3u} orbital. These results are also in line with recent investigations on a larger number of [2.2]cyclophanes[9]. In Table 1 the experimental and theoretical ionization potentials of **2** are compared.

Table 1. Comparison between the recorded vertical ionization potentials, $I_{v,j}$, of **2** with the calculated orbital energies ε_j. All values in eV

band	$I_{v,j}$	assignment [5]	$- \varepsilon_j$(MINDO/3)
①	7.9	"$^2B_{3u}$"	7.62
② ⎱	8.1	⎰ "$^2B_{2g}$"	8.43
③ ⎰		⎱ "$^2B_{3g}$"	8.77
④	9.5	"$^2B_{2u}$"	9.53

The different orbital sequence for **1** and **2** should have an impact on the e.s.r. spectra of the corresponding radical cations. For **1**$^+$ the spin density in the $^2B_{2g}$ ground state is predicted to be localized in the aromatic rings, for **2**$^+$, however, a $^2B_{3u}$ ground state is expected and thus large coupling constants with the H atoms of the aliphatic bridge are predicted.

Experimental Part

The He(I) PE spectrum of **2** has been recorded on a PS18 spectrometer (Perkin Elmer, Beaconsfield, England) at 110°C. The spectrum was calibrated with Xenon and Argon. A resolution of 20 meV on the Argon line was obtained.

[1] R. Gleiter, Tetrahedron Lett. **1969**, 4453.
[2] E. Heilbronner and J. P. Maier, Helv. Chim. Acta **57**, 151 (1974).
[3] E. A. Truesdale and R. S. Hutton, J. Am. Chem. Soc. **101**, 6475 (1979).
[4] R. Gleiter, Top. Curr. Chem. **86**, 197 (1979), and references therein.
[5] Although **2** belongs to pointgroup C_{2h} we use the same irreducible representations as for **1**.
[6] T. Koopmans, Physica **1**, 104 (1934).
[7] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Am. Chem. Soc. **97**, 1255 (1975); P. Bischof, ibid. **98**, 6844 (1976). – The calculations have been carried out with program MOPN (Quantum Chem. Prog. Exch. **12**, 383 (1979)).
[8] R. Hoffmann, A. Imamura, and W. Hehre, J. Am. Chem. Soc. **90**, 1499 (1968); R. Hoffmann, Acc. Chem. Res. **4**, 1 (1971); R. Gleiter, Angew. Chem. **86**, 770 (1974); Angew. Chem., Int. Ed. Engl. **13**, 696 (1974); E. Heilbronner and A. Schmelzer, Helv. Chim. Acta **58**, 936 (1975).
[9] B. Kovač, M. Allan, and E. Heilbronner, Helv. Chim. Acta **64**, 430 (1981).

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