# $\pi-\pi$-Interactions in Pentacyclo-[8.2.1.1.$^{2,5}$1.$^{4,7}$1$^{8,11}$]hexadeca-1,7-diene

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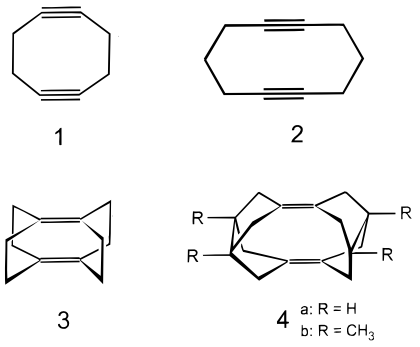
If two $\pi$-systems, such as two triple or two double bonds, are separated by ethano or propano bridges, a considerable difference between the energy splitting of the molecular $\pi$ orbitals is encountered. This difference is apparent in comparing the photoelectron spectra of 1,5-cyclooctadiyne (**1**) and 1,6-cyclodecadiyne (**2**).[1] The splitting of the ionization energies of the "in-plane" $\pi$-orbitals in these diynes was found to be 0.4 eV for **1** and 1.5 eV for **2**.[1]




A similar difference is expected in dienes in which the double bonds are connected by four ethano and four propano bridges. An example of the former type of diene is provided by tricyclo[4.2.2.2$^{2,5}$]dodecadiene-1(2),5(6) (**3**),[2] and pentacyclo [8.2.1.1$^{2,5}$1.$^{4,7}$1$^{8,11}$]hexadeca-1,7-diene (**4a**)[3] and its 4,5,10,11-tetramethyl derivative **4b**[4] provided examples of the latter. To demonstrate the existence of the predicted difference in the $\pi$-orbital energies in **3** and **4**, we have recorded the He(I) photoelectron (PE) spectra of **4a** and **4b** and compared the spectra with that of **3**.[5]

The PE spectrum of **4a** (Figure 1) shows two bands at 7.43 and 8.97 eV (see Table 1) which are well separated from strongly overlapping bands at higher energies. The

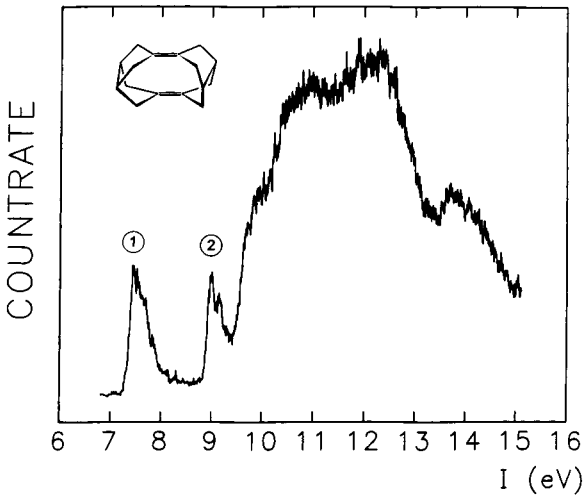



**Figure 1.** PE spectrum of **4a**.

**Table 1. Vertical Ionization Energies (eV), $I_{v,j}$, and Calculated (-$\epsilon_j$, ΔSCF, ΔMP2) Ionization Energies (eV) of 4a**

| band | $I_{v,j}$ | assignment | -$\epsilon_j$[a] | ΔSCF[b] | ΔMP2[c] | state |
|---|---|---|---|---|---|---|
| 1 | 7.43 | $8b_{2u}$ $\pi^-$ | 7.85 | 6.74 | 7.24 | $1\ ^2B_{2u}$ |
| 2 | 8.97 | $11a_g$ $\pi^+$ | 9.62 | 8.55 | 8.67 | $1\ ^2A_g$ |

[a] RHF/6-31G*//RHF/6-31G*. [b] R(U)HF/6-31G*//RHF/6-31G*. [c] R(U)MP2/6-31G*//RHF/6-31G*.

PE spectrum of **4b** looks very similar, and the first two bands appear at 7.32 and 8.79 eV.

To interpret the PE spectra of **4a** and **4b**, we have carried out quantum chemical calculations on **4a**. The geometry of **4a** was optimized in $D_{2h}$ symmetry at the Hartree−Fock level of theory, using the 6-31G* basis set.[6] A frequency calculation showed that the optimized $D_{2h}$ geometry is a minimum on the potential energy surface for **4a**. The predicted ionization energies were obtained, both from application of Koopmans's theorem[7] and by ΔSCF and ΔMP2 calculations (see Table 1). In the ΔSCF energy calculations we used the RHF method for the neutral molecule, and the UHF methology for the radical cation and its excited states. Thus, ΔMP2 uses the RMP2 method for **4a** but its unrestricted version (UMP2) for the cations. All these single-point calculations were carried out at the RHF geometry of the neutral molecule **4a**. The electronic structure of **4a** was further investigated by partitioning the interactions between the localized $\pi$ bonds into those through-space (TS) and those through-bond (TB).[8] We make use of a methodology, first suggested by Heilbronner and Schmelzer,[9] which is based on the Fock matrix in a localized basis. For a quantitative treatment we applied the procedure of Imamura et al.[10] It is based on subsequent diagonalization steps of those parts of the Fock matrix which correspond to the relevant localized orbitals. As a

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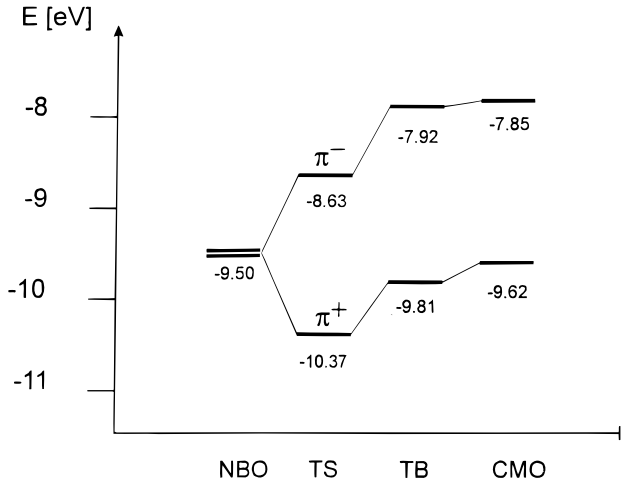


**Figure 2.** Interaction diagram of **4a**. NBO: energy of the degenerate noninteracting $\pi$-MOs; TS: energy after through-space interaction; TB: energy after through-bond interaction; CMO: energy of the canonical MOs.

starting point for our analyses we used Weinhold's natural bond orbitals[11] (NBO).[12]

## Results

In Figure 2 we show how our calculations predict the orbital energies of the $\pi$-bonds and are affected by through-space and through-bond interactions. The localized $\pi$-orbitals (NBO) are split symmetrically by their through-space (TS) interaction. This effect is quite large, despite the distance of 3 Å between the atomic centers, because there is a relatively strong overlap between the orbitals, due to their face-to-face orientation. TS mixing is calculated to result in the $\pi^+$ combination lying 1.74 eV below the $\pi^-$ combination. Next, we take into account the TB interaction of the $\pi$ orbitals due to their mixing with the orbitals of the C−C $\sigma$ frame. This leads to an overall rise of both orbital energies, which are now calculated by the Imamura procedure to be very close to the canonical Hartree−Fock orbital energies (CMO). The calculations show that the TB interaction involves largely the bonds of the C−C skeleton, not the C−H bonds.

Four combinations of C−C $\sigma$ bonds belong to the same $A_g$ representation as $\pi^+$ and three belong to the same $B_{2u}$ representation as $\pi^-$. However, using arguments from second-order perturbation theory[14] only those orbitals which are energetically close to each other will interact effectively. Of the above seven C−C skeletal orbitals, two are predicted at about −13 eV all others are below −16 eV and should therefore not interact strongly with $\pi^+$ at −9.8 or $\pi^-$ at −7.9 eV.

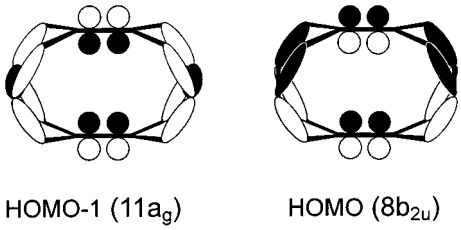


**Figure 3.** Schematic drawing of the two highest occupied canonical MOs **4a**.

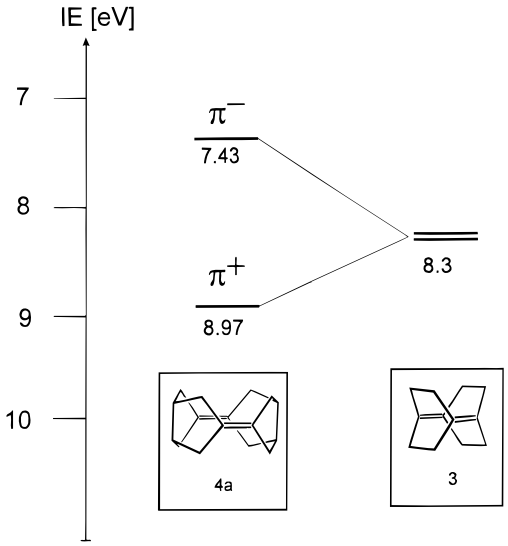


**Figure 4.** Correlation between the first two bands of the PE spectra of **3** and **4a**.

The HOMO and HOMO-1 of **4a** consists of the out of phase combination of, respectively, the $b_{2u}$ skeletal orbital and $\pi^-$ and the $a_g$ skeletal orbital and $\pi^+$ (Figure 3). Nevertheless, both the HOMO and HOMO-1 have a very high degree of $\pi$ character, 77% in the former and 81% in the latter.

## Conclusion

Since both $\pi^+$ and $\pi^-$ interact strongly with the C−C $\sigma$ bonds, the large splitting due to the through-space splitting is maintained.

In contrast to the PE spectra of **4a** and **4b** that of **3** shows only a minute splitting between the bands arising from $\pi^+$ and $\pi^-$ (see Figure 4). The TS splitting in **3** was calculated[5] to be comparable to that in **4a**. However, the TS splitting in **3** is compensated for by interaction of only $\pi^+$ with the $\sigma$ skeleton, while $\pi^-$ has no partner in the $\sigma$ frame to interact with. Consequently, unlike the case in **4**, where the $\sigma$ bonds interact with both $\pi^+$ and $\pi^-$ so that their TS splitting is maintained, in **3** the destabilization of only $\pi^+$ by TB interactions almost exactly compensates for the TS splitting between $\pi^+$ and $\pi^-$ leading to a PE spectrum that is very different in appearance from that of **4a** and **4b**.

## Experimental Section

The He(I) spectra of **4a**[3] and **4b**[4] were recorded with a PS18 spectrometer (Perkin-Elmer) at room temperature. The calibration was performed with Ar and Xe. A resolution of 20 meV on

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the $P3_{/2}$ Ar line was obtained. The MO calculations were carried out with the Gaussian 94 program.[13]

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**Supporting Information Available:** Table of calculated Cartesian coordinates for the optimized geometry of **4a** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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