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# Electronic Structure of Spiropentane and Some Derivatives[†]

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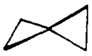
The He I photoelectron (PE) spectra of spiropentane (1), tricyclo[4.1.0.0$^{1,3}$]heptane (2), and 4,5-benzotricyclo[4.1.0.0$^{1,3}$]hept-4-ene (3) have been recorded. The assignment of the first bands is based on molecular orbital calculations using MNDO and ab initio methods. A qualitative MO model for the valence orbitals of 1 is suggested.

Spiropentane (1) is the simplest saturated spiro hydrocarbon. In connection with thermolysis reactions,[1] spectroscopic investigations of heterospiropentane-derivatives with lone pairs,[2] and earlier investigations on [3]rotane[3] and other highly strained hydrocarbons,[4] we were interested in the valence molecular orbitals (MOs) of 1 and its congeners tricyclo[4.1.0.0$^{1,3}$]heptane (2) and 4,5-benzotricyclo[4.1.0.0$^{1,3}$]hept-4-ene (3). The method of choice to investigate the sequence of the highest occupied MOs is by means of He I photoelectron (PE) spectroscopy, provided that we can assume that the negative values of the calculated orbital energies ($-\epsilon_j$) can be set equal to the measured vertical orbital energies ($I_{v,j}$) (Koopmans' approximation[5]).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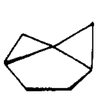
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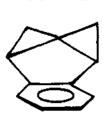
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In this paper we first derive the valence molecular orbitals (MOs) of 1 in a qualitative manner and compare its result with PE spectroscopic investigations on 1–3, together with molecular orbital calculations using semiempirical and ab initio methods.

**MO Scheme of 1.** The spiropentane skeleton can be constructed starting from a central carbon atom and two ethylene fragments interacting with each other. The basis orbitals of the carbon atom are 2s, $2p_x$, $2p_y$, and $2p_z$ while the two peripheral fragments contribute with their $\pi$ and $\pi^*$ MOs.

In Figure 1 we show the interaction diagram for 1. On the left side the orbital energies of the carbon 2s and 2p atomic orbitals are shown. On the right side the linear combinations of the $\pi$ and $\pi^*$ MOs are drawn adopting $D_{2d}$ symmetry. For reasons of symmetry, all four linear combinations of the ethylene fragments ($a_1$, $b_2$, e) interact with the AOs of the carbon giving rise to four bonding and four antibonding Walsh-type valence orbitals of spiropentane.

Three of the four highest occupied valence orbitals are expected to be at low energy due to their p character, while the fourth one ($a_1$) shows strong 2s character. In a semilocalized picture all four MOs correspond to the four C–C bonds between the central carbon atom and the peripheral $CH_2$ units. A schematic drawing is provided in Figure 2.

**Table I. Comparison between the Recorded Vertical Ionization Energies ($I_{v,j}$) of 1 and the Predicted Orbital Energies ($\epsilon_j$) Using the MNDO and the ab Initio Level Employing Different Basis Sets (All Values in eV)**

| band | $I_{v,j}$ | assignment | $-\epsilon_j$ (MNDO) | $-\epsilon_j$ (STO-3G) | $-\epsilon_j$ (4-31G) |
|---|---|---|---|---|---|
| 1 | 9.73 | $3b_2$ | 11.01($b_2$) | 9.60($b_2$) | 10.60($b_2$) |
| 2 | 10.4 | 3e | 11.17(e) | 10.23(e) | 11.22(e) |
| 3 | 10.9 | | | | |
| 4 | 12.25 | $1a_2$ | 12.70($a_1$) | 12.36($a_1$) | 13.35($a_2$) |
| 5 | 12.85 | $3a_1$ | 12.96($a_2$) | 12.68($a_2$) | 13.42($a_1$) |
| 6 | 13.1 | $1b_1$ | 13.11($b_1$) | 13.08($b_1$) | 13.87($b_1$) |
| 7 | 15.8 | 2e | 15.76(e) | 16.40(e) | 17.22(e) |
| 8 | 16.0 | | | | |
| 9 | 16.2 | $2b_2$ | 16.14($b_2$) | 16.85($b_2$) | 17.65($b_2$) |

**Table II. Comparison between the Recorded Vertical Ionization Energies of 2 and 3 and the Predicted Orbital Energies ($\epsilon_j$) Using the MNDO and the ab Initio Method Employing a STO-3G Basis (All Values in eV)**

| compd | band | $I_{v,j}$ | assignment | $-\epsilon_j$ (MNDO) | $-\epsilon_j$ (STO-3G) |
|---|---|---|---|---|---|
| 2 | 1 | 9.15 | 10a | 10.19 | 7.94 |
| | 2 | 9.7 | 9b | 10.46 | 8.43 |
| | 3 | 10.3 | 8b | 11.07 | 9.48 |
| | 4 | 11.3 | 9a | 11.90 | 10.93 |
| | 5 | 11.7 | 7b | 12.54 | 11.55 |
| | 6 | 12.0 | 8a | 12.88 | 11.80 |
| | 7 | 13.0 | 7a | 13.75 | 14.18 |
| 3 | 1 | 8.2 | 13b($\pi$) | 9.02 | 6.60 |
| | 2 | 8.8 | 14a($\pi$) | 9.30 | 7.19 |
| | 3 | 9.6 | 13a($\sigma$) | 10.51 | 8.70 |
| | 4 | 10.4 | 12b($\sigma$) | 10.78 | 9.29 |
| | 5 | 10.7 | 11b($\sigma$) | 11.53 | 10.46 |

**PE Spectra of 1–3.** To check our simple Walsh-type picture of the valence MOs of 1 as well as the conjugative interactions in 3, we have investigated the PE spectra of 1–3. The spectra are shown in Figure 3 and the first ionization energies are collected in Table I. The spectrum of 1 shows three close-lying bands below 11.5 eV in the ratio of 1:1:1. These bands are followed by another triplet between 12 and 13.5 eV which is separated by a large gap from a broad band around 16 eV. Bodor et al.[6] recorded the PE spectrum of 1 with an early, low-resolution PE spectrometer; the present high-resolution data provide

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[†] Dedicated to Professor Marianne Baudler on the occasion of her 65th birthday.

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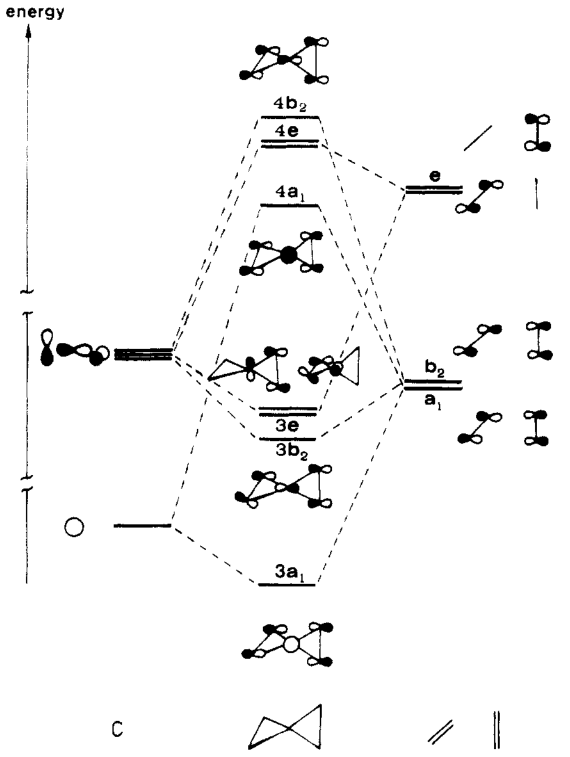

**Figure 1.** Qualitative interaction diagram between the AOs of a carbon atom (left) and the $\pi$ MOs of two ethylenes (right) to yield the valence MOs of spiropentane.

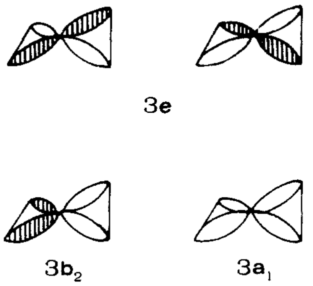

**Figure 2.** Semilocalized representation of the highest occupied MOs of spiropentane.

more bands resolved and more accurate band positions.

A similar appearance is encountered for the PE spectrum of **2**. The only difference is that the first six bands are shifted by 0.6–1.1 eV to lower ionization energies. Thus the $C_2H_4$ bracket acts purely inductively (Table II). The PE spectrum of **3** shows five bands between 8 and 11 eV. In order to assign them empirically, we have compared them with those of 1,2,3,4-tetrahydronaphthaline[7] and **1** in Figure 4. This comparison clearly shows that the first two bands in the PE spectrum of **3** are due to ionizations from $\pi$ MOs of the benzene fragment, while bands 3–5 should be assigned to ionization events from the Walsh-type MOs of the spiropentane fragment. This comparison furthermore shows that there is essentially no interaction between the valence MOs of the spiropentane moiety and the benzene part.

**MO Calculations.** To test our qualitative MO picture of **1** and our empirical assignments of the PE spectra of **1**–**3**, we have carried out MO calculations on **1**–**3**. The methods used were the MNDO method[8] and the restricted Hartree-Fock theory employing a STO 3G basis for **1**–**3** and for **1** a 4-31 G basis.[9]

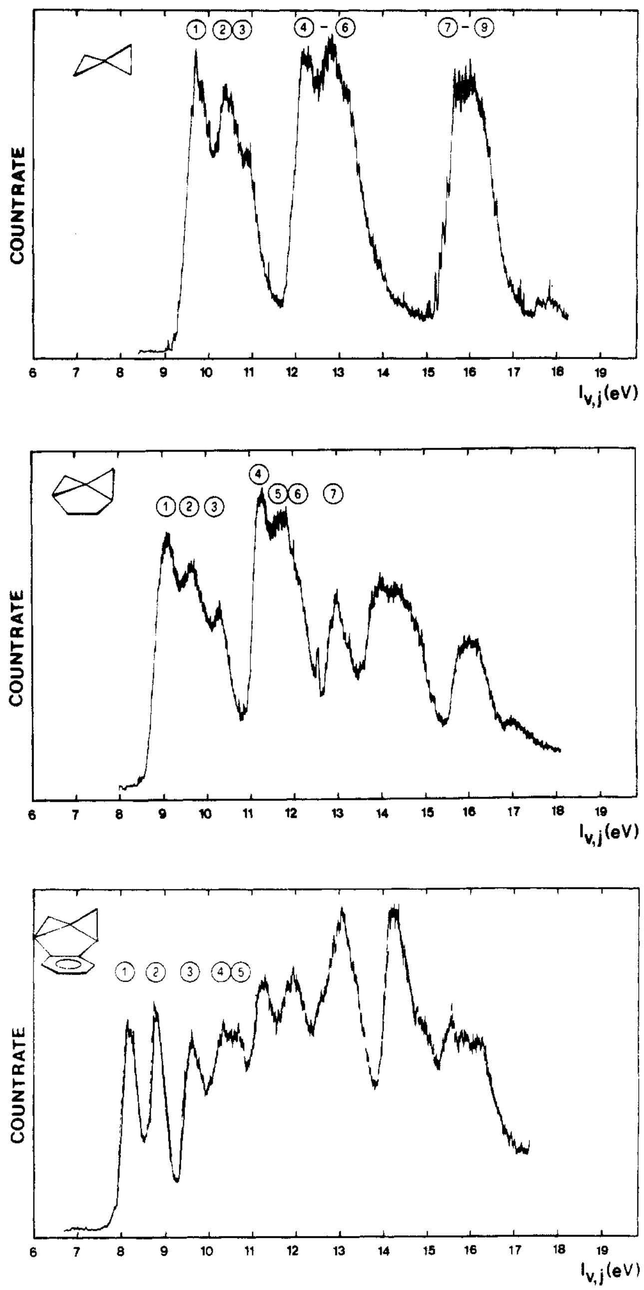

**Figure 3.** He I PE spectra of **1**–**3**.

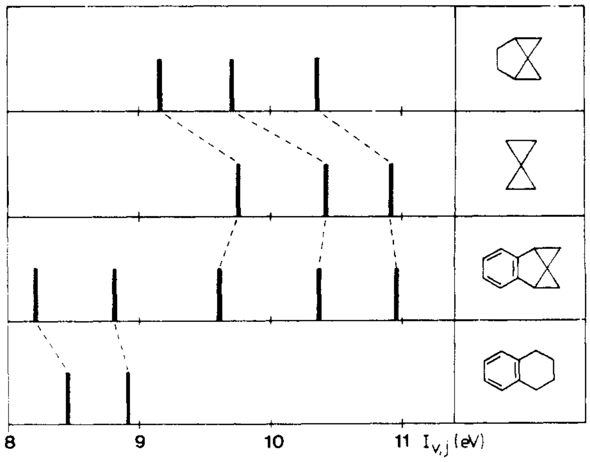

**Figure 4.** Comparison between the first bands of **1**–**3** and those of 1,2,3,4-tetrahydronaphthalene.

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**Table III. Geometrical Parameters Used for the MO Calculations on 1-3**

| | C(1)-C(2) | C(2)-C(3) | C(3)-C(4) | C(4)-C(5) | C(1)-C(3) | C(4)-C(8) | C(8)-C(9) | C(9)-C(10) |
|---|---|---|---|---|---|---|---|---|
| **1** | 1.469 | 1.519 | 2.265 | 1.519 | 1.469 | | | |
| **2** | 1.465 | 1.526 | 1.521 | 1.500 | 1.519 | | | |
| **3** | 1.510 | 1.498 | 1.503 | 1.447 | 1.564 | 1.897 | 1.415 | 1.400 |

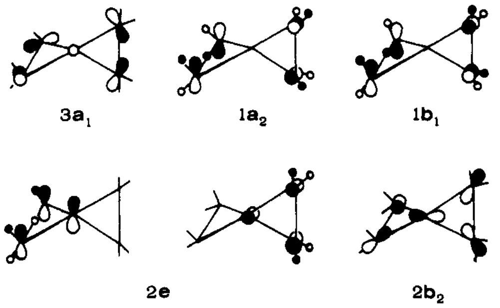

**Figure 5.** Schematic representation of the MOs of **1** predicted at lower orbital energies.

For **1** we adopted the geometrical parameters reported by electron diffraction studies.[10] The orbital energies obtained for **1** using the MNDO procedure and the basis sets mentioned above are given in Table I. All procedures reproduce the experiment in so far as the valence MOs consist of three groups each containing three MOs. The highest occupied three MOs (Figures 1, 2) can be derived by linear combinations of the C-C bonds which originate from the central atom. The following two groups can either be described as linear combinations of the two peripheral C-C bonds ($3a_1$, $2b_2$) with proper C-H admixtures or as linear combinations of the C-H $\sigma$ bonds. In the latter case the linear combinations $1a_2$, $1b_1$, and 2e result. It is interesting to note that $1a_2$ and $1b_1$ are split due to spirointeraction.[11] All six MOs just discussed are shown schematically in Figure 5. The bond distances found for **1** are relatively close to those calculated by ab initio[12] and force field[13] methods. The geometrical parameters derived by the MNDO method are less satisfactory because the peripheral C-C bonds are predicted as too short and the central C-C bonds as too long.

If we adopt for **2** the geometrical parameters obtained by electron diffraction measurements,[14] the splitting pattern observed in the PE spectrum is not reproduced. The gap observed between bands 3 and 4 is not found. An analysis of the corresponding MOs reveals that a $\sigma$ MO strongly localized in the C(4)-C(5) bond is shifted at too high orbital energy. Shortening the relative long C(4)-C(5) bond to 1.50 Å gives a much better agreement between experiment and calculation (see Table II) in so far as two groups of close-lying MOs are obtained each group consisting of three MOs. The results for **2** listed in Table II are based on the electron diffraction parameters for **2**, except for the bond length of C(4)-C(5) for which we adopted a value of 1.50 Å. The main effect of the $C_2H_4$ bridge in **2** is a shift of the six highest occupied valence MOs as indicated in Figure 4. The large discrepancy between the predicted PE pattern and the calculated one when adopting a bond length of 1.572 Å for the C(4)-C(5) bond led us to suggest that one should reexamine the electron diffraction data for **2**.[14] The geometrical parameters reported for **2** and adopted in this work are given in Table III.

For **3** our results are based on the geometrical parameters predicted by the MNDO procedure (Table III). Both methods of calculations applied predict two $\pi$ MOs of the benzene moiety on top of three $\sigma$ orbitals related to 3e and $3b_2$ of the spiropentane moiety.

## Experimental Section

The He I photoelectron spectra of the analytically pure compounds have been recorded on a Leybold-Heraeus UPG 200 spectrometer at room temperature. The spectra have been calibrated with Ar and Xe. A resolution of 25 meV on the $^2P_{3/2}$ Ar line was obtained.

The preparation of **1**,[15] **2**,[16] and **3**[17] has been reported in the literature.

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**Registry No.** **1**, 157-40-4; **2**, 174-73-2; **3**, 74410-87-0.

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