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A PHOTOELECTRON SPECTROSCOPIC STUDY OF PROXIMITY EFFECTS IN 8,11-DISUBSTITUTED PENTACYCLO(5.4.0.0$^{2.6}$.0^{3,10}.0^{5,9})UNDECANES

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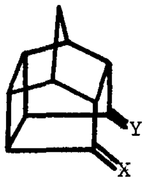
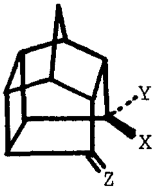
SUMMARY: Photoelectron spectra of six 8,11-disubstituted pentacycloundecanes (**1**, **3** - **7**) are reported; the results suggest that the through-space interaction betweeen unsaturation centers in **1** and **3** dominates over the through-bond interaction mechanism.

Shen and Kuebler[1] have reported the photoelectron (PE) spectra of **1** and **2**, below. Whereas a single *pi*-ionization of 9.10 eV was observed for **2**, two such ionizations were found for **1** (8.50 and 8.90 eV). The 0.4 eV splitting in the PE spectrum of **1** *vis-à-vis* the lack of splitting observed in the corresponding spectrum of **2** was taken as evidence for the operation of a significant through-bond interaction between the *pi*-systems associated with the 8,11-methylene units in **1**.



1: X = Y = CH$_2$
4: X = CH$_2$; Y = O
5: X = CHCl; Y = O
6: X = Y = O



2: X = CH$_3$; Y = H; Z = CH$_2$
3: X = Y = H; Z = CH$_2$
7: X = Y = H; Z = O

Inspection of molecular models suggests that considerable steric congestion exists in **2** due to the proximity of the *endo*-11 methyl group to the carbon-carbon double bond in the 8-position. Hence, **2** might not be an ideal model "monoene" for judging the mechanism of transmission of the *pi*-*pi* interaction in **1**. Accordingly, we have reexamined this question using the less congested model system **3**.

Additionally, we have considered the question of the existence or nonexistence of 1,6-(lone pair-lone pair) interactions in the corresponding dione (**6**) and 1,4-pi-pi interactions in the enone (**4**) system. Compound **7** was chosen as a "monoketone" model system for comparison with **6**, Compound **5** was used to assign the PE bands in **4**. The syntheses of **3**[2], **4**[2], **6**[3], and **7**[2] in our laboratory have been reported elsewhere.[4]

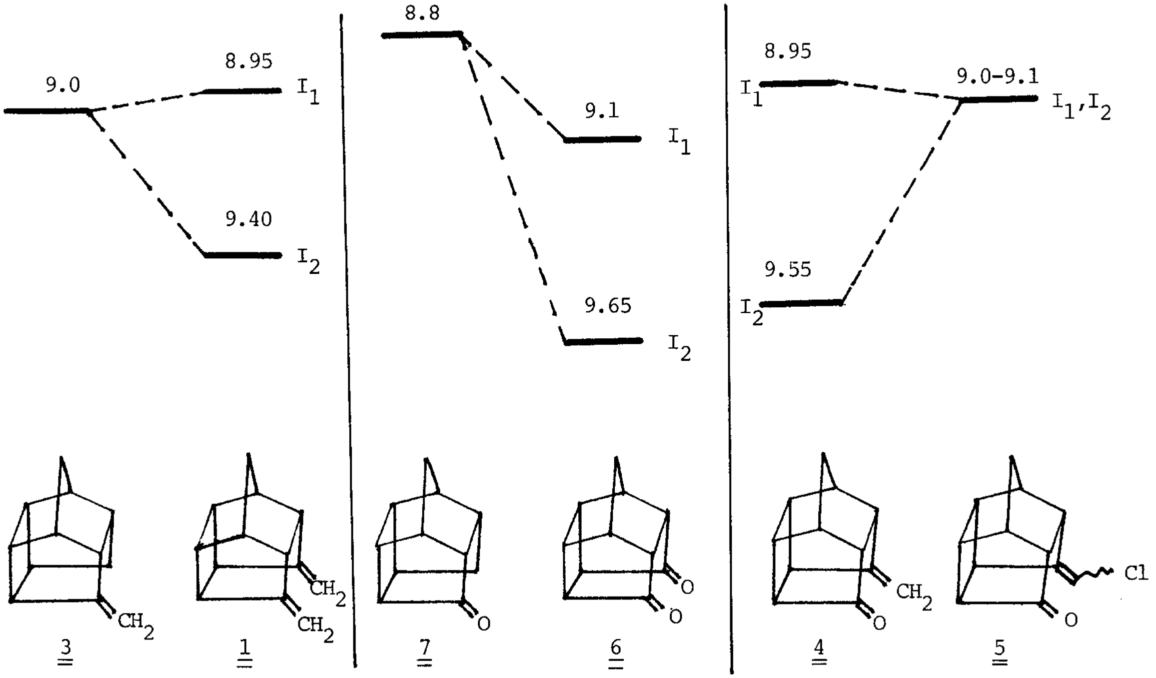
The pi-ionization potentials which we observed for compounds **1** and **3-7** appear in the Table. Several important points emerge from consideration of the data in this Table. First, our absolute value for I_1 and I_2 in compound **1** differ considerably from the corresponding values reported by Shen and Kuebler[1], although the magnitudes of the splitting (I_2-I_1) found in **1** are very similar in the two studies. Interestingly, the pi-ionization potential for **3** (9.0 eV) is identical to that reported by Shen and Kuebler[1] for **2**. However, when an interaction diagram for **1** similar to that published by Shen and Kuebler [1] is prepared (see Figure), we arrive at the conclusion that the through-space interaction mechanism dominates over a through-bond mechanism, whereas they reached the opposite conclusion for this compound.[5]

Comparison of the ionization potential values obtained for **6** and **7** in this study is instructive. Again, the PE spectrum displays a single value for the n_O-ionization potential of the monofunctionalized compounds (**7**), while the PE spectrum of the difunctionalized compound (**6**) reveals pronounced splitting, (I_2-I_1=0.55 eV). As was the case for the situation cited above for **1**, we find for **6** that the through-space interaction mechanism dominates over a through-bond mechanism.

Comparison of the pi-ionization potential values which we obtained for **4** and **5** similarly affords interesting conclusions. The PE spectrum of enone **4** reveals pronounced splitting, (i.e., (I_2-I_1 = 0.60 eV). However, when a chlorine atom is placed on the carbon-carbon double bond (which is the situation in **5**), the ionization potentials I_1 and I_2 merge. The value of I_1 in **5** (vis-à-vis I_1 in **4**) appears to be relatively unaffected by the presence of chlorine on the carbon-carbon double bond. This observation suggests that I_1 in **4** can be assigned to ionization from one of the nonbonding orbitals on the oxygen atom.[6] However, the value of I_2 in **5** is drastically diminished relative to that in **4**. Since the most pronounced

FIGURE

Orbital Energy Differences Obtained by PE Spectroscopy



TABLE

Vertical *Pi*-Ionization Potentials (eV) Obtained from PE Spectra

COMPOUND	I_1	I_2
1	8.95	9.40
3	9.0	
4	8.95	9.55
5	9.0-9.1	
6	9.1	9.65
7	8.8	

effect of the chlorine substituent should be felt by the carbon-carbon bond, we can assign I_2 in **4** to vertical ionization from $\pi_{C=C}$.

Our results confirm the existence of a 1,4-pi-pi interaction in **1**, although we disagree with the conclusions of Shen and Kuebler[1] regarding the relative importance of through-bond coupling in **1**. The situation regarding 1,4-pi-pi interactions in enone **4** is less clear-cut owing to the inherent asymmetry of the system, (i.e., 1,5-n-pi interactions must be explicitly considered in this compound). The pronounced substituent effect of chlorine on the PE spectrum of **5** has proved useful in assigning the bands in the PE spectrum of **4**. However, clarification of the nature and extent of the pi-pi interaction in **4** awaits the results of detailed molecular orbital calculations which are in progress.

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REFERENCES AND FOOTNOTES

1. K.-W. Shen and N. A. Kuebler, *Tetrahedron Lett.*, 2145 (1973).

2. A. P. Marchand and R. Kaya, *J. Org. Chem.*, *49*, 0000 (1984).

3. A. P. Marchand and R. W. Allen, *J. Org. Chem.*, *39*, 1596 (1974).

4. The synthesis of **5**, mp 106.5-107.8°C, will be published elsewhere; IR (film) 3060(w), 2990(s), 2947(m), 2880(w), 1733(vs), 1665(w), 1315(m), 1278(m), 1230(m), 1085(w), 1050(w), 915(m), 825(m) and 767 cm^{-1}(m); Proton NMR ($CDCl_3$) AB pattern, J_{AB} = 11 Hz, δ_A 1.66 (1H), δ_B 1.96 (1H), δ 2.36-3.74 (m, 8H), δ5.80 (s, 1H); C-13 NMR ($CDCl_3$) 36.84(d), 38.79(t), 42.47(d), 43.34(d), 44.59(d), 45.78(d), 48.05(d), 49.03(d), 54.01(d), 107.86(d), 143.29(s), 215.61(s). *Anal.* Calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.37. Found (Galbraith Laboratories, Inc.) C, 69.87; H, 5.39.

5. Shen and Kuebler[1] have based their suggestion that through-bond interaction is dominant in **1** on their observation that both pi-ionization potentials for this diene were lower than the pi-ionization of their monoene model (**2**). This result could only be interpreted in terms of dominant through-bond interaction between the 1,4-pi-systems in **1**. However, in the present study we find that the two pi-ionization potentials of diene **1** bracket that of our monoene model, **3**; this is exactly what would be expected for a through-space interaction.

6. D. Chadwick, D. C. Frost, and L. Weiler, *J. Am. Chem. Soc.*, *93*, 4320, 4962 (1971).

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