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n,π-Interactions in Polycyclic Unsaturated Ketones: Photoelectron Spectroscopic Study

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He I photoelectron spectra (PE) of several β,γ-unsaturated polycyclic ketones, their parent ketones, and alkenes have been measured. The assignment of spectra is based on semiempirical MO calculations (PM3 method) and empirical arguments. *Endo*-derivatives showed larger HOMO/SHOMO band separation than *exo-cyclic* unsaturated ketones. The results of MO calculations are in good agreement with this general trend. Strikingly different photochemical transformations and $\pi^* \Leftarrow n$ electronic transition intensities, exhibited by the two groups of compounds, can be rationalized within the framework of oxygen lone pair $\leftrightarrow$ π bond interactions.

Introduction

Polycyclic β,γ-unsaturated ketones undergo different photochemical transformations depending on the relative position of the two chromophore groups (C=C, C=O). Besides reactions typical of ketones and alkenes, the bischromophoric reactions (1,3- and 1,2-acyl shifts), also occur.[2] The observed increase in intensity of a normally weak (symmetry forbidden) $\pi^* \Leftarrow n$ electronic transition further supports the hypothesis of a significant interaction between π_{cc} and n_o orbitals.

In this work we have attempted to find an explanation for such a behavior based on differences in electronic structure. The photoelectron spectroscopy together with standard MO calculations was used to probe the electronic structure. PE and UV spectra of parent polycyclic alkenes and ketones were also measured in order to facilitate the analysis.

Experimental Section

Derivatives of protoadamantane (**1**–**6**),[3,4] adamantane (**7**–**9**),[5] brendane (**10**–**11**),[6] and homoadamantane (**12**–**14**)[7] were prepared according to the published procedures. UV spectra were recorded on Pye-Unicam SP 8-100 spectrophotometer (10^{-3} M in EtOH).

The He I PE spectra of compounds **1**–**14** were recorded on a Vacuum Generators UV-G3 spectrometer[8] under 25-meV resolution. The sample inlet system was heated up to 30–70 °C in order to generate sufficient vapor pressure in the ionization region. PE spectra were calibrated by adding small amounts of Ar and Xe to the sample gas flow. The spectra are shown in Figures 1–5 and the numerical results are presented in Table 1.

Standard MOPAC 6.0 program package (QCPE 455) and PM3 Hamiltonian were used in the calculations. The molecular geometries were fully optimized using EF algorithm with the final energy gradient being < 0.01. Input geometries were optimized initially with a molecular mechanics (MM2) method.

Results and Discussion

Intramolecular orbital interactions are a useful concept for understanding numerous phenomena: molecular conformations, reactivities, UV, CD and ESR spectral variations.[9] Photoelectron spectroscopy had been particularly useful in probing such interactions, especially in the case of unsaturated ketones.[10–12]

The work reported so far, often involved studies of polycyclic (bi)ketones containing multiple double bonds. In the present work we wished to investigate simpler compounds containing a single π and a single CO group, the relative positions of which vary within the polycyclic alkane skeleton.

Two electronic systems, $\tilde{X}$ and $\tilde{A}$ with ionization energies (E_i) < 10 eV are invariably observed in the spectra of unsaturated ketones: **2**, **4**, **6**, **8**, **11**, and **13**. They correspond to carbonyl oxygen lone pair (n_o) and double bond (π) ionizations. The π labeling, of course, has meaning only in terms of local symmetry, since all molecules (except **7** and **9**) belong to C_1 point group. This assignment can be readily verified by comparison with the spectra of parent ketones and alkenes: **1**, **3**, **5**, **7**, **9**, **10**, **12**, and **14** (Figures 1–5). The spectra show that n_o systems are generally narrow, having poorly resolved vibrational fine structure (if any), while the π systems are broader, exhibiting well resolved vibrational progressions. In relation to that, $\tilde{X}$ and $\tilde{A}$ systems in unsaturated ketones display different profiles; $\tilde{A}$ is narrower and asymmetric with steeper onset (except in **13** where the situation is reversed). The difference indicates that in asymmetric profile 0–0 vibrational transition is the strongest, which can be taken as an indication of an underlying nonbonding orbital character. System contours can thus be used to attribute MO character to HOMOs and SHOMOs. This tends to suggest that $\tilde{X}$ should be ascribed to MO with π,

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Table 1. PE Vertical (adiabatic) Ionization Energies (E_i/eV), Unsaturated Ketone $n_o - \pi_{cc}$ Separations (ΔE/eV), HOMO and SHOMO PM3 Orbital Energies (MO/eV), UV Absorption Maxima (λ/nm), and Molar Absorption Coefficients (ϵ/M^{-1} cm^{-1}) for the Title Compounds

	E_i			MO			
compound	$\tilde{X}$	$\tilde{A}$	ΔE	HOMO	SHOMO	λ	ϵ
1	8.83 (8.68)	10.15	–	10.25 n_o	11.25 σ	294	28
2	8.69	9.57	0.88	9.8 ($\pi_{cc} - n_o$)	10.62 ($\pi_{cc} + n_o$)	302	139
3	8.85 (8.68)	9.95	–	9.74 π_{cc}	10.99 σ	212	1430
4	8.5	9.61	1.10	9.8 ($\pi_{cc} - n_o$)	10.8 ($\pi_{cc} + n_o$)	294	200
5	8.82 (8.69)	10.3	–	10.28 n_o	11.43 σ	284	55
6	8.67	9.55	0.88	9.90 ($\pi_{cc} - n_o$)	10.69 ($\pi_{cc} + n_o$)	284	310
7	9.0 (8.67)	10.2	–	10.23 n_o	11.35 σ	286	20
8	8.74	9.53	0.79	9.93 ($\pi_{cc} - n_o$)	10.63 ($\pi_{cc} + n_o$)	292	106
9	8.83 (8.65)	9.8	–	9.83 π_{cc}	10.95 σ	208	526
10	8.95 (8.8)	10.75	–	10.27 n_o	11.62 σ	292	30
11	8.60	9.76	1.16	9.76 ($\pi_{cc} - n_o$)	10.86 ($\pi_{cc} + n_o$)	299	148
12	8.98 (8.87)	10.05	–	10.4 n_o	11.3 σ	287	26
13	8.88	9.31	0.42	10.14 n_o	10.44 π_{cc}	290	39
14	8.81 (8.66)	9.7	–	9.75 n_o	10.98 σ	211	1110

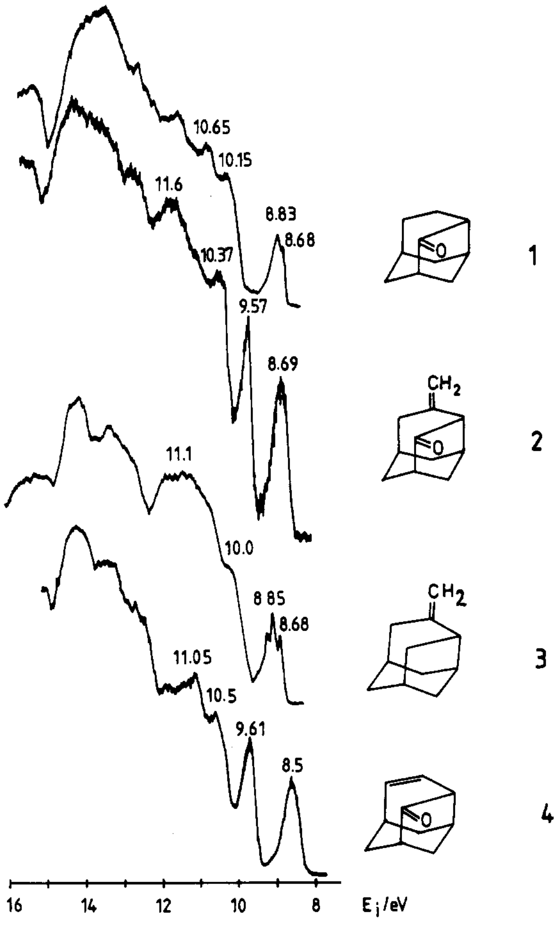

Figure 1. He I PE spectra of protoadamantane derivatives 1–4.

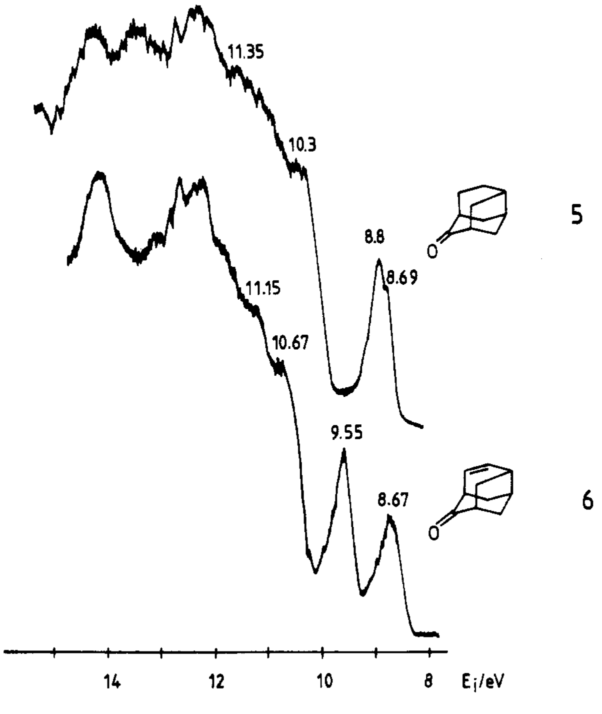

Figure 2. He I PE spectra of protoadamantane derivatives **5** and **6**.

and $\tilde{A}$ to MO with n_o character, except in **13** where the reverse description should apply. The true picture is, however, more complex. The loss of vibrational fine structure in unsaturated ketones, especially in $\tilde{X}$ (π system), indicates that n_o and π orbitals mix (interact). The mixing entails delocalization, which in turn leads to smaller vibrational level spacings and the subsequent loss of fine structure. The strength of 1,4-n,π-interactions can be gauged from the difference $\Delta E = E_i(\tilde{A}) - E_i(\tilde{X})$; it is strongest in **11** and weakest in **13** (where 1,5-n,π-interactions are active). The interaction is generally stronger in *endo* than in *exo* derivatives (Table 1, see ΔE values).

The reverse must also hold true i.e. the appearance of fine structure indicates decreased mixing. These assumptions are confirmed by the spectra. In the unsaturated ketones the fine structure disappears only to reappear again in **13**. The n_o/π interaction in **13** is small, as can be seen from the reduced $\tilde{X}$–$\tilde{A}$ separation. The small interaction in **13** can be expected, due to a larger number of σ bonds separating the chromophores.

The endo C=C bond is better placed (compared to exo C=C) for overlap with carbon σ skeleton orbitals which act as a vehicle for through-bond (TB) n_o,π-interactions. The through-space interactions (TS) do take place as well. ΔEs in **4** and **11** (both *endo* derivatives) are 1.11 and 1.16 eV, respectively. However, *endo*-derivative **6** and *exo*-derivatives **2** and **8** have significantly lower ΔEs of 0.88, 0.88, and 0.79 eV, respectively. TB interactions in all molecules (except **13**) are of 1,4-n,π-type. The different ΔEs must than be attributed to varying extent of TS interactions. Both TB and TS, of course, contribute to the measured ΔE gaps.

The experimental results show that only β,γ-unsaturated ketones **4**[13] and **11**[6] undergo photochemical bischromophoric reactions: oxa-di-π-methane rearrangement and

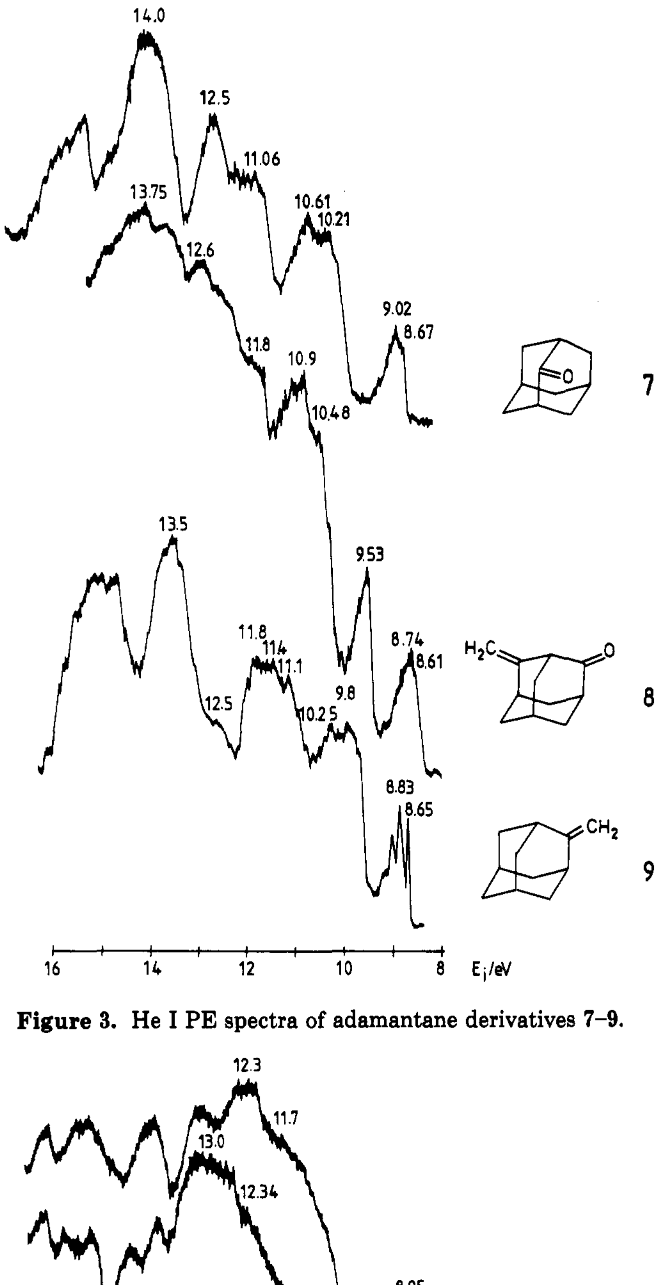

Figure 3. He I PE spectra of adamantane derivatives 7–9.

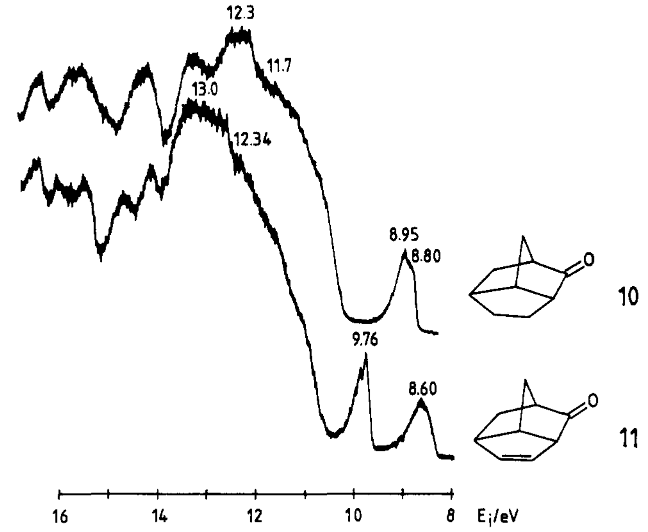

Figure 4. He I PE spectra of brendane derivatives 10 and 11.

1,3-acyl shift. In contrast, the unsaturated ketones 2[4] and 8,[14] under the same reaction conditions, gave products characteristic of simple alkenes or ketones. Thus, it appears that TS interactions can best be rationalized in terms of the different chemical behavior of 4 and 11 vs 2 and 8. MO calculations indicated that in the unsaturated ketones, $\tilde{X}$ and $\tilde{A}$ systems correspond to out-of-phase ($\pi_{cc} - n_o$) and in-phase ($\pi_{cc} + n_o$) MOs, respectively. The relative contributions of the π_{cc} and n_o components vary and can be estimated from the PE spectra. In 2, 4, 6, 8, and 11, HOMO has an excess of π_{cc}, while SHOMO has more n_o character. 13 is an exception in reverse i.e. HOMO has more n_o and SHOMO more π_{cc} character. We can test the "experimentally derived" MO characters by examining the molar absorption coefficients (ϵ) for lowest energy electronic transitions in the UV spectra (Table 1). Should HOMO have significant π_{cc} character its ϵ value will be larger than if it had n_o character. The reason for the difference is that $\pi^* \Leftarrow n$ transitions are forbidden by selection rules while $\pi^* \Leftarrow \pi$ transitions are allowed and strong. Inspection of Table 1 confirms that our hypothesis is correct; ketones have $\epsilon < 60$ M^{-1} cm^{-1}, unsaturated ketones $\epsilon > 100$ M^{-1} cm^{-1}, and cycloalkenes $\epsilon > 500$ M^{-1} cm^{-1}. Homoadamantane derivative 13 is an exception, being the only unsaturated ketone with a low ϵ value. This can however be understood if one remembers that HOMO in 13 has more n_o than π character. The reason for the HOMO character exception can possibly be due to preferential n_o–σ over π–σ orbital interactions.

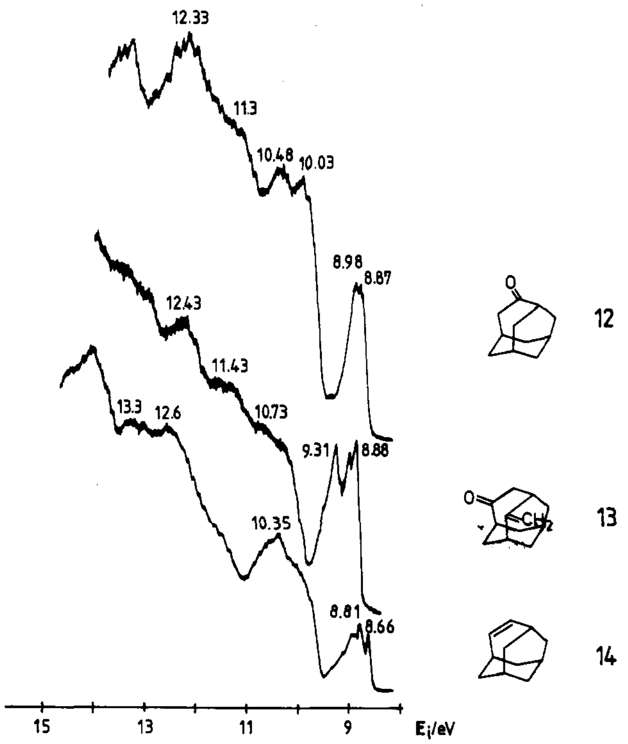

Figure 5. He I PE spectra of homoadamantane derivatives 12–14.

Another important detail in the spectral variations concerns $\tilde{X}$ system profiles in the spectra of ketones 1, 5, and 10. The profiles, deriving undoubtedly from n_o ionizations, are broader than one might expect of a lone pair (nonbonding orbital), and furthermore 0–0 transition is not the most intense one. And yet, in the corresponding unsaturated ketones 2, 4, and 11 the related $\tilde{A}$ system has a narrower width and a distinctly strongest 0–0 transition. There appears to be a paradox: a lone pair orbital experiences, upon n_o/π mixing, band narrowing and 0–0 transition intensity enhancement. A plausible explanation lies in the fact that n_o in ketones[15] is in fact mixed with

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spatially extensive σ orbitals of the bicyclic system which gives it its uncharacteristic shape. In unsaturated ketones n_0 can mix with either π or σ orbitals. C_1 symmetry imposes no restrictions, so the mixing takes place predominantly with π orbitals which are close in energy. The π orbitals are, on the other hand, much less delocalized than σ which leads to relative band narrowing and 0–0 intensity enhancement. LUMO energies in unsaturated ketones do not vary much as can be seen from small variation in UV absorption wavelengths (Table 1). One must emphasize that due to demonstrated HOMO–SHOMO orbital mixing, any consideration of chemical reactivities,[16,17] within the framework of frontier MO theory, should include both orbitals and not just HOMO as is the usual practice.

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