

Photoelectron Spectra and Electronic Structure of Some Steroids

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Dedicated to Professor C. Sandorfy on the Occasion of his 65th Birthday

Gas phase HeI photoelectron spectra of 5 α -androstane, 5 α -androstan-3-one and 5 α -androstan-17-one compared with those of other saturated cyclic hydrocarbons and ketones indicated that the electronic effect of a keto group in steroids is rather local i.e. extending over about two rings.

Steroids, readily available, stable and stereochemically defined compounds have repeatedly been used in research of chemical reaction mechanisms. Thus, they enabled for instance the study of stereochemical aspects and long range effect of groups at specified distances from reactive centers of chemical reactions. The discussion of these results in terms of conformational and/or electron distribution changes was so far scarcely supported by quantum chemical calculations and not at all with results on electronic structure as obtained from photoelectron (PE) spectroscopy. Possibly that size of the molecules and lack of experience with this class of compounds played a role in inhibiting quantum chemists towards this field, since only a few attempts to predict their charge distribution and conformations are known [1–4].

Concerning PE spectroscopy we report here the first spectra of the steroids; 5 α -androstane (**1**) and two of its keto-derivatives 5 α -androstan-3-one (**2**) and 5 α -androstan-17-one (**3**) recorded with HeI excitation under low resolution (Fig. 1) and those of the low energy part of **2** and **3** under high resolution (Figure 2). Chemically, androstane is a saturated polycyclic hydrocarbon molecule substituted with two methyl groups, Me-19 and Me-18 at bridgehead positions 10 and 13, respectively. It has a relatively rigid and strainless molecular structure [5]: ring A can change from α to β configuration, methyl groups

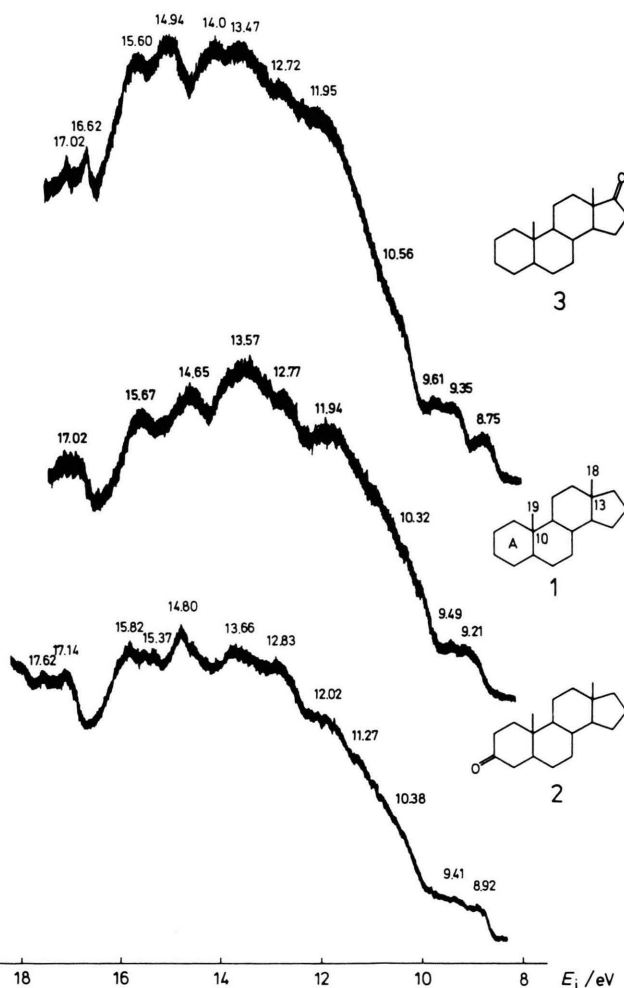


Fig. 1. Low resolution (FWHM about 50 meV) HeI photoelectron spectra of 5 α -androstan-17-one (top) and 5 α -androstan-3-one (bottom) with indicated values of vertical ionization energies $E_{i,v}$.

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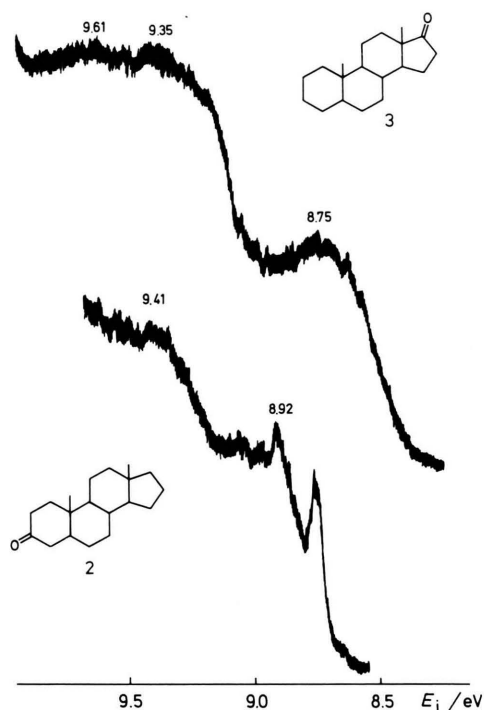


Fig. 2. Low energy part of HeI photoelectron spectra of 5 α -androstan-17-one (upper) and 5 α -androstan-3-one (lower) recorded under high resolution (FWHM about 20 meV).

can rotate (Me-19 faster than Me-18) [6] and the five membered ring slightly change conformations.

The PE spectrum of **1** shows more pronounced peaks than one of a saturated chain hydrocarbon [7] but less than that of a more rigid tetracyclic adamantoid hydrocarbon [8]. Two nearly overlapping band systems appear at the low energy side of the spectrum with vertical ionization energies of 9.21 and 9.49 eV. Lacking any better description even for much smaller hydrocarbon molecules (e.g. cyclohexane, where the lowest ionizations occur at 10.32 and 10.93 eV) [7] we accordingly assign both these systems to mixed π_{CH_2} , σ_{CC} ionizations. Besides that the keto group is together with the hydroxy and methyl groups the biologically most important substituent in steroid chemistry, it also exhibits a characteristic electronic effect wellknown from PE spectra of saturated cyclic ketones [9]: a strong shift of the σ -ionizations of the parent hydrocarbon to higher energy (> 1 eV). This interaction can be explained as stabilizing the hydrocarbon's

σ_{CC} and σ_{CH} on account of a destabilization of the oxygen lone pair electrons. Thus, usually a gap is observed in the PE spectra of cyclic ketones between the band corresponding to the n_O and those to the σ -onset ionizations. The effect is evident also in polycyclic ketones (e.g. 2-adamantanone¹) and is doubled if two distant keto groups are present in the molecule (e.g. 2,6-adamantandione¹) [8]. Since in these polycyclic ketones (adamantanones, noradamantanones, protoadamantanones and homonoradamantanones) the (through bond) distance of a keto group to any carbon atom in the molecule never exceeds four C–C bonds, one can conclude that over a distance of two rings the effect is pronounced and additive in nature.

Can it be traced also over the four rings of a steroid molecule? It is clear from Fig. 1 that this “ σ -shifting” effect is very small in the present pairs androstane/androstanone.

A number of examples of long range effects of a substituent group on chemical processes in steroids and related molecules exist in the literature and have been interpreted in terms of conformational, inductive (“through bond”) and field (“through space”) effects acting either alone or in combination. The importance of the nature of these long range effects in steroids is not limited only to their influence on reactivity: since small changes in steroid structure lead to changes in their activity, the knowledge of substituent effect transmission is fundamental for understanding their biochemistry as well. Especially conclusive concerning the transmission of the substituent effect in steroids are nmr studies of changes of chemical shifts on substitution [10–13]. Results for androstanones e.g. indicate that all positions in androstane are affected by a single keto group [11–13], however, the effect is also strongly decreasing at a distance greater than two rings. On the other hand intramolecular electron transfer (ET) over fixed distances of several “insulating” σ -bonds has recently shown to occur on the ns or even ps time scale [14–17]. In the case of such transfer between two electron binding (keto) groups separated by 7–11 Å in steroids [18], experiments carried out in organic glasses at 77 K with

¹ The O–O band of the \tilde{X} system in the PE spectra of adamantane at 9.28 eV has to be compared with the σ -onset in 2-adamantanone at about 10.0 eV and 2,6-adamantandione at about 10.7 eV.

pulse radiolysis techniques, to create trapped electrons which were captured by a group on one end of the molecule, indicated that the ET process is much faster than the 100 ns time resolution. However, solvation energies had a remarkable influence on the extent and direction of ET. Thus, here it is also an open problem whether the mode of interaction is mainly through space or through bond. PE spectroscopy measuring these electronic effects in the gas phase, in the case of steroids will mainly show the through bond interaction. From PE spectra of several steroids with a keto group in various distance it should be possible to evaluate the range and possibly magnitude of their electronic interaction. This work is in progress. In conclusion, the present results would indicate that the electronic effect of one keto group in steroids is hardly observed but introduction of another keto (or other "transmitting") group in a distance of two or more rings could make it extending over the whole molecule.

Experimental

5 α -androsterane, 5 α -androstan-3-one and 5 α -androstan-17-one were of commercial origin, high purity and were used without further purification. The PE spectra were recorded on a Vacuum Generators UVG3 instrument at 80, 130 and 140 °C, respectively, using the HeI line for excitation [19]. The energy scale was calibrated by admitting MeI and/or Ar to the sample flow.

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