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Photoelectron Spectra, MNDO Calculations and Electronic Structure of Some Saturated Steroids

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Photoelectron (PE) spectra in conection with semiempirical MNDO SCF MO calculations (assuming validity of Koopmans' theorem) and empirical arguments (*i. e.* composite molecule method) are used to derive (valence) electron structure of 5α-androstane (*1*), 5α-androstan-3-one (*2*), 5α-androstan-11-one (*3*), 5α-androstan-17-one (*4*), 5α-androstane-3,17-dione (*5*) and 5α-androstane-3,11,17-trione (*6*).

INTRODUCTION

In the past years we have been interested in PE spectra of steroids.[1–3] Steroids, a group of allicyclic compounds containing a perhydrogenated cyclopentanophenanthrene (»sterane« or »gonane«) as a basic structural characteristic, play a variety of biological roles in humans. They are components of bile, brain, spinal tissue and some of them are sexual hormones. In a number of cases, the mechanism of hormone action involves interaction with specific receptors in cellular plasma membranes and subsequent generation of intracellular secondary messengers (such as cyclic-AMP, cyclic-GMP, diacylglycerol, calcium ion *etc.*). In other words, the information that is inherent in an extracellular hormone is transfered and amplified by an intracellular mediator for that hormone. Steroid hormones utilize a different mechanism of information transfer.[4–6] Essential steps in induction of a biological response are the binding of a hormone to a receptor protein present in a target cell and the interaction of the receptor-protein complex with nuclear chromatin. The precise details of this interaction and the role played by the steroid in this process are still unknown. But molecular structure (*i. e.* composition, configuration, conformation) and electronic properties (*i. e.* energy, electron distribution) undoubtedly have a direct bearing upon receptor affinity and directly or indirectly influence receptor activation, transport and nuclear interaction. The structural factor is well documented. From the comparison of the three-dimensional structures and binding affinities of the steroid hormones, their agonists and antagonists, it is possible to deduce structural characteristics compatible with binding to the protein, while from the knowledge of the amino-acid sequence and predicted secondary structure of the protein it is possible to identify putative binding sites by modeling and/or graphic techniques. On the other hand, our knowledge about the electronic structure of steroids, both by quantum chemistry and PE spectroscopy, is very sparse. Thus, elucidation of (valence) electronic structure of steroids is essential for the better understanding of their biochemistry.

Mainly because of their well defined stereochemistry, steroids have been widely used in the study of cooperative long-range substituent effects (through space *vs.* through bond) at distances fixed by an inert spacer — steroid framework. But recent studies on intramolecular electron-transfer (ET) processes in molecular systems in which donor and acceptor groups are separated by 5α-androstane[7] (or by some other saturated polycyclic hydrocarbon[8]) question that long-standing hypothesis about the inertness of the basic steroid skeleton. The theoretical and experimental evidences suggest that the coupling between donor and acceptor in these systems is provided by the interaction with the frontier orbitals of the intervening molecular fragments. It follows that the »ribbon-like« orbitals of saturated polycyclic hydrocarbons can »conduct« electrons over ten or even more single CC bonds, although more experimental evidence is needed. In this context, the informations provided by PE spectroscopy and/or quantum chemical calculations are of crucial importance.

In this work, we investigate the long-range interactions of carbonyl groups located at the biologically important 3- and/or 11- and/or 17- positions of steroid framework. The information about the type and extent of interactions between them, as well as on MO symmetries, is provided by the MNDO calculations. This method gives a qualitatively correct description of the valence electronic structure of these molecules.

EXPERIMENTAL AND CALCULATIONS

The HeI PE spectra of compounds *1*, *2* and *4*—*6* were recorded on a Vacuum Generators UV-G3 spectrometer[9] at 80, 130, 140, 170 and 180 °C, respectively, using MeI and/or Ar and/or Xe as calibrants in admixture with the compound. Compounds were of commercial origin and were used without further purification.

Standard semiempirical MNDO SCF MO calculations were performed for all compounds using the QCPE 464 (IBM MOPAC) program[10] adapted for the Siemens 7580S (turbo-version) at the Computing center of the University of Düsseldorf. Full geometry optimization was obtained for 11-one and 3,11,17-trione, while for the other measured compounds single geometry calculations were performed. Input data were chosen on the basis of crystallographic data[11] and standard values of bond lengths and angles (r_{CC} = 154 pm, r_{CH} = 108 pm, r_{CO} = 122.5 pm, $\sphericalangle$CCC = 109.5° and 120.0°, $\sphericalangle$CCH = 109.5°, $\sphericalangle$COC = 120.0°).

RESULTS AND DISCUSSION

The MNDO energies and assignment for the oxygen lone pair of compounds *1*—*6* are compared to the corresponding PE ionization energies (Table I). This comparison is being made on the assumption that the overall shape of the observed PE spectrum could be obtained, after appropriate scaling, by replacing each orbital eigenvalue by a Gaussian of width 0.250—0.300 eV.[12] The non-zero (>0.001) eigenvectors for the six highest occupied MO's of the same molecules are given in Table II.

TABLE I

Canonical orbital energies, ε_i^{MNDO}/eV, for the thirty highest occupied levels in 5α-androstane derivatives 1—6 and measured ionization energies (I_p/eV)

	1		2		3	4		5		6	
	ε^{MNDO}	I_p	ε^{MNDO}	I_p	ε^{MNDO}	ε^{MNDO}	I_p	ε^{MNDO}	I_p	ε^{MNDO}	I_p
HOMO	-10.975	9.21	-10.532	8.92 n_O	-10.367 n_O	-10.376	8.75n_O	-10.453	8.94n_O	-10.474	8.90n_O
2nd	-11.127	9.49	-11.191	9.41	-11.209	-11.339	9.35	-10.601	9.06n_O	-10.618	9.09n_O
3rd	-11.515		-11.447		-11.313	-11.548	9.61	-11.511	9.82	-11.059	9.50n_O
4th	-11.552	10.32	-11.698		-11.698	-11.733		-11.721	10.18	-11.919	
5th	-11.756		-11.908	10.38	-11.819	-11.791	10.56	-11.906		-12.085	10.28
6th	-11.819		-12.034		-11.948	-11.950		-12.188	10.75	-12.243	
7th	-12.006		-12.060		-12.243	-12.210		-12.233		-12.381	10.48
8th	-12.143		-12.196		-12.374	-12.241		-12.429		-12.472	
9th	-12.187	11.94	-12.346		-12.449	-12.410		-12.718	11.09	-12.813	10.94
10th	-12.336		-12.470	11.27	-12.552	-12.551		-12.787		-12.905	
11ht	-12.417		-12.632		-12.718	-12.603	11.95	-12.943		-12.983	
12th	-12.529		-12.724		-12.766	-12.694		-12.989		-13.151	12.38
13th	-12.604		-12.797		-12.801	-12.797		-13.031	12.33	-13.167	
14th	-12.691	12.77	-12.881	12.02	-12.877	-12.876		-13.139		-13.278	
15th	-12.709		-12.993		-12.967	-13.003		-13.229		-13.415	12.64
16th	-12.875		-13.176	12.83	-13.090	-13.136	12.72	-13.447		-13.493	
17th	-12.962		-13.410		-13.349	-13.203		-13.558		-13.659	
18th	-13.260	13.57	-13.565		-13.404	-13.489		-13.711	13.34	-13.757	
19th	-13.469		-13.671	13.66	-13.599	-13.753		-13.784		-13.900	13.77
20th	-13.562		-13.711		-13.825	-13.930	13.47	-13.910		-14.009	
21st	-13.748	14.65	-13.855		-13.987	-14.033		-14.007	13.89	-14.255	
22nd	-13.861		-13.942	14.80	-14.062	-14.089		-14.169		-14.357	14.82
23rd	-13.984		-14.045		-14.184	-14.187		-14.356		-14.449	
24th	-14.124		-14.306		-14.209	-14.395	14.0	-14.399		-14.576	
25th	-14.347	15.67	-14.395	15.37	-14.313	-14.598		14.565	15.02	-14.728	15.77
26th	-14.396		-14.627		-14.615	-14.860		-14.607		-14.758	
27th	-14.442		-14.728	15.82	-14.652	-14.965	15.60	-14.806	16.00	-15.074	
28th	-14.944		-15.135	17.14	-14.932	-15.151		-15.299		-15.444	
29th	-15.111	17.02	-15.316		-15.202	-15.335	17.02	-15.377	17.34	-15.521	17.29
30th	-15.141		-15.474	17.62	-15.397	-15.610		-15.558		-15.581	

The highest occupied »ribbon-like« MO's are considered to intervene in long-range effects which are taking part in large polycyclic hydrocarbons. Being formed from C2p AO's aligned along molecular axes, HOMO and SHOMO of 5α-androstane (Figure 1) have the highest electron density on two inner rings carbon atoms. According to the alignment of the constituent C2p AO's they can be classified as transversal (T-type; HOMO) and longitudinal (L-type; SHOMO) orbitals. The characteristic feature of these orbitals is electron density spread over the whole system, therefore being described as a mixture of σ_{CC} and π_{CH_2} orbitals. The pseudo π_{CH_2} nature of methylene electrons is shown to be essential for transmission of electronic effects in substituted polycyclic hydrocarbons.[13] High electron density in the middle of the molecular frame would have significant influence on C2p AO's interactions if we were to alter the original structure of B and/or C rings (*i. e.*, by interpolation of double bonds[3,14]).

Substitution of methylene group by keto group brings about notable changes in the electronic structure of the parent molecule. There is a pro-

TABLE II

The non-zero (>0.001) MNDO eigenvectors for the six highest occupied MO's of compounds 1—6

5α-Androstane

ε_i/eV	-10.975	-11.127	-11.515	-11.552	-11.756	-11.819
sC_1	-0.028	-0.030	0.020	-0.031	-0.015	-0.010
p_xC_1	-0.042	0.195	-0.018	-0.066	0.060	-0.098
p_yC_1	-0.115	-0.149	-0.010	-0.169	0.047	0.045
p_zC_1	0.077	0.152	-0.113	0.102	0.152	0.049
sC_2		0.022	0.006	0.006	0.008	-0.013
p_xC_2	0.082	-0.163	0.004	0.120	-0.047	0.086
p_yC_2	0.074	0.067	0.027	0.166	-0.057	-0.068
p_zC_2	-0.033	-0.067	0.060	-0.078	-0.155	-0.058
sC_3	0.005	-0.013	0.006	0.004	-0.029	-0.002
p_xC_3	-0.060	0.120	-0.002	-0.073	0.069	-0.099
p_yC_3	-0.076	-0.099	-0.025	-0.187	0.027	0.086
p_zC_3	0.030	0.065	-0.045	0.085	0.176	0.061
sC_4	-0.030	0.014	0.008	-0.025	-0.019	-0.015
p_xC_4	0.139	-0.203	-0.010	0.099	-0.036	0.140
p_yC_4	0.080	0.085	0.038	0.172	-0.018	-0.099
p_zC_4	-0.017	-0.054	0.068	-0.054	-0.200	-0.082
sC_5	0.019		0.027	0.012	-0.026	-0.022
p_xC_5	-0.151	0.181	-0.015	-0.134	0.053	-0.123
p_yC_5	-0.235	-0.132	-0.118	-0.255	0.043	0.114
p_zC_5	0.031	0.071	-0.115	0.056	0.229	0.108
sC_6	-0.034	-0.009	0.013	-0.020	-0.022	-0.002
p_xC_6	0.109	-0.188	0.008	-0.068	-0.077	0.079
p_yC_6	0.149	0.122	0.054	0.101	0.071	-0.047
p_zC_6	-0.037	-0.088	0.093	-0.088	-0.139	-0.040
sC_7	0.025	0.027	0.026	-0.036	0.018	-0.010
p_xC_7	-0.156	0.150	-0.031	0.060	0.021	-0.096
p_yC_7	-0.194	-0.110	-0.100	0.115	-0.090	-0.011
p_zC_7	0.029	0.071	-0.104	0.047	-0.007	0.010
sC_8	-0.014	-0.019	0.045	0.011	0.024	-0.002
p_xC_8	0.166	-0.215	-0.024	-0.041	-0.019	0.010
p_yC_8	0.197	0.184	0.069	-0.116	0.051	0.034
p_zC_8	-0.085	-0.121	0.270	-0.011	0.148	0.002
sC_9	-0.027	0.015	0.044	-0.026	0.005	-0.008
p_xC_9	-0.166	0.283	-0.023	-0.139	-0.015	-0.082
p_yC_9	-0.190	-0.187	-0.107	0.070	0.032	-0.044
p_zC_9	0.093	0.090	-0.267	-0.002	-0.053	0.002
sC_{10}		0.021	0.028	0.003	-0.022	0.001
p_xC_{10}	0.178	-0.281	-0.031	0.134	-0.029	0.023
p_yC_{10}	0.223	0.156	0.138	0.255	-0.078	-0.116
p_zC_{10}	-0.077	-0.092	0.213	-0.115	-0.195	-0.075
sC_{11}	0.023	0.022	0.032	0.015	-0.018	0.037
p_xC_{11}	0.150	-0.131	0.013	0.023	0.124	-0.192
p_yC_{11}	0.192	0.098	0.154	0.006	-0.064	0.137
p_zC_{11}	-0.064	-0.042	0.144	0.040	0.097	-0.022
sC_{12}	-0.036	0.016	0.011	0.022	0.014	-0.010
p_xC_{12}	-0.082	0.166	0.004	-0.068	-0.141	0.196
p_yC_{12}	-0.157	-0.052	-0.064	0.153	0.050	-0.161
p_zC_{12}	0.080	0.032	-0.101	-0.128	-0.131	0.032
sC_{13}	0.010	-0.010	0.016	-0.007	0.017	0.012
p_xC_{13}	0.181	-0.127	-0.053	-0.160	0.185	-0.328
p_yC_{13}	0.232	0.058	0.085	-0.283	0.036	0.191
p_zC_{13}	-0.101	-0.032	0.139	0.128	0.183	0.039
sC_{14}		0.027	0.034	-0.031	0.030	0.004
p_xC_{14}	-0.178	0.212	0.039	0.031	0.007	-0.043
p_yC_{14}	-0.248	-0.040	-0.027	0.318	-0.098	0.001
p_zC_{14}	0.076	0.026	-0.190	-0.038	-0.218	-0.012

5α-Androstan-3-one

ε_i/eV	-10.532	-11.191	-11.447	-11.699	-11.908	-12.034
sC_1	0.028	0.016	-0.030	0.016	-0.030	0.031
p_xC_1	0.051	0.008	0.162	-0.025	-0.006	-0.103
p_yC_1	0.117	0.061	-0.103	0.009	-0.132	0.089
p_zC_1	-0.034	-0.056	0.132	-0.076	0.136	-0.158
sC_2	-0.082	0.019	0.009		-0.026	0.003
p_xC_2	-0.122	-0.028	-0.158	0.012	0.041	0.076
p_yC_2	-0.346	0.029	-0.030	0.001	-0.021	0.014
p_zC_2	0.003	0.017	-0.051	0.026	-0.065	0.081
sC_3		-0.006	-0.015	0.002	0.006	0.015
p_xC_3	-0.009	0.017	0.039	-0.001	-0.030	-0.030
p_yC_3	0.242	-0.010	0.014	-0.003	-0.011	0.009
p_zC_3	-0.102	0.004	-0.005	-0.006	0.014	-0.010
sC_4	0.084	0.015	0.047		-0.006	-0.024
p_xC_4	0.133	-0.124	-0.133	0.007	0.139	0.044
p_yC_4	-0.236	-0.017	-0.040	0.022	0.060	-0.022
p_zC_4	0.244	-0.030	0.047	0.022	0.050	-0.041
sC_5	-0.019	-0.016	-0.013	0.019	0.019	-0.002
p_xC_5	-0.066	0.111	0.130	-0.023	-0.139	-0.044
p_yC_5	0.107	0.174	-0.060	-0.091	-0.273	0.179
p_zC_5	-0.063	-0.014	0.028	-0.064	-0.018	-0.035
sC_6	0.032	0.026	0.013	0.006	-0.016	
p_xC_6	0.081	-0.127	-0.143	0.019	0.019	0.123
p_yC_6	-0.093	-0.121	0.060	0.064	0.120	-0.117
p_zC_6	0.079	0.013	-0.031	0.070	-0.059	0.043
sC_7	-0.014	-0.030	0.023	0.028	-0.031	-0.005
p_xC_7	-0.052	0.165	0.116	-0.052	-0.020	-0.100
p_yC_7	0.038	0.209	-0.112	-0.127	0.044	0.046
p_zC_7	-0.020	-0.026	0.059	-0.107	0.084	-0.019
sC_8	0.002	0.017	-0.015	0.048	-0.006	-0.020
p_xC_8	0.016	-0.177	-0.248	-0.003	0.029	0.122
p_yC_8	-0.036	-0.208	0.204	0.093	-0.018	-0.057
p_zC_8	0.019	0.087	-0.119	0.283	-0.120	-0.030
sC_9	0.005	0.017	0.008	0.042	-0.024	0.008
p_xC_9	-0.007	0.142	0.299	-0.049	-0.144	-0.060
p_yC_9	0.035	0.192	-0.212	-0.095	-0.056	0.018
p_zC_9	-0.022	-0.096	0.098	-0.250	0.056	-0.029
sC_{10}		0.006	0.030	0.022	0.005	
p_xC_{10}	0.009	-0.161	-0.304	-0.015	0.143	0.045
p_yC_{10}	-0.090	-0.156	0.097	0.101	0.272	-0.183
p_zC_{10}	0.045	0.058	-0.051	0.156	-0.123	0.126
sC_{11}	-0.004	-0.015	0.025	0.030	0.038	0.019
p_xC_{11}		-0.153	-0.168	0.017	-0.016	-0.195
p_yC_{11}	-0.032	-0.179	0.117	0.149	0.131	0.066
p_zC_{11}	0.014	0.071	-0.053	0.150	0.029	-0.056
sC_{12}		0.041	0.010	0.012	0.016	-0.032
p_xC_{12}	-0.007	0.080	0.209	-0.005	-0.009	0.213
p_yC_{12}	0.011	0.186	-0.094	-0.078	0.053	-0.191
p_zC_{12}	-0.005	-0.105	0.053	-0.125	-0.121	0.149
sC_{13}	0.002	-0.009	-0.010	0.021	0.001	0.006
p_xC_{13}	0.004	-0.217	-0.162	-0.053	-0.242	-0.270
p_yC_{13}	-0.013	-0.275	0.119	0.131	-0.180	0.220
p_zC_{13}	0.007	0.137	-0.045	0.195	0.133	-0.110
sC_{14}	-0.004	-0.005	0.028	0.037	-0.039	-0.003
p_xC_{14}	-0.016	0.183	0.241	0.007	-0.046	-0.124
p_yC_{14}	0.011	0.304	-0.093	-0.060	0.278	-0.048
p_zC_{14}	-0.001	-0.098	0.035	-0.223	0.063	0.134

5α-Androstan-11-one

ε_i/eV	-10.376	-11.339	-11.548	-11.733	-11.791	-11.950
sC_1	-0.006	-0.037	-0.039	0.002	0.018	-0.005
p_xC_1	-0.034	0.212	-0.110	-0.087	0.076	-0.030
p_yC_1	-0.067	-0.207	-0.135	-0.172	0.053	0.028
p_zC_1	0.018	0.178	0.121	-0.124	-0.108	0.087
sC_2	-0.006	0.021	-0.002	0.012	0.005	-0.009
p_xC_2	0.055	-0.155	-0.160	0.110	-0.100	0.032
p_yC_2	0.079	0.124	0.112	0.187	-0.057	-0.039
p_zC_2	-0.005	-0.098	-0.084	0.120	0.110	-0.133
sC_3	0.003	-0.013	0.011	0.029	0.002	-0.014
p_xC_3	-0.029	0.131	-0.143	-0.091	0.069	-0.003
p_yC_3	-0.034	-0.173	-0.105	-0.183	0.069	0.020
p_zC_3	0.009	0.087	0.069	-0.119	-0.107	0.141
sC_4	-0.016	0.002	-0.034	0.008	0.015	-0.010
p_xC_4	0.076	-0.200	0.200	0.048	-0.070	-0.003
p_yC_4	0.034	0.154	0.077	0.147	-0.055	0.001
p_zC_4	-0.003	-0.072	-0.062	0.161	0.093	-0.118
sC_5	0.027	0.006	-0.012	0.037	0.004	-0.007
p_xC_5	-0.092	0.169	-0.201	-0.103	0.086	-0.006
p_yC_5	-0.148	-0.214	-0.142	-0.279	0.032	-0.043
p_zC_5	0.001	0.088	0.100	-0.208	-0.097	0.066
sC_6	-0.010	-0.026	-0.039	0.007	0.003	-0.007
p_xC_6	0.029	-0.196	0.137	0.172	0.100	-0.021
p_yC_6	0.060	0.188	0.102	0.082	0.022	0.110
p_zC_6	-0.009	-0.118	-0.094	0.111	0.083	0.020
sC_7	0.025	0.021	-0.019	-0.011	0.038	0.024
p_xC_7	-0.069	0.153	-0.156	-0.002	-0.110	-0.032
p_yC_7	-0.118	-0.105	-0.017	0.037	-0.173	-0.131
p_zC_7	0.015	0.068	0.069	-0.070	-0.025	-0.122
sC_8	-0.014	-0.011	-0.008	0.019	-0.004	0.046
p_xC_8	0.050	-0.161	0.180	-0.014	0.125	0.009
p_yC_8	0.119	0.167	0.009	-0.032	0.164	0.107
p_zC_8	-0.030	-0.092	-0.120	0.089	-0.005	0.280
sC_9	0.059	0.001	-0.086	-0.009	0.001	0.011
p_xC_9	-0.211	0.246	-0.126	-0.024	0.116	-0.058
p_yC_9	-0.295	-0.147	0.132	0.074	-0.064	0.045
p_zC_9	-0.012	0.065	0.153	-0.063	-0.003	-0.118
sC_{10}	-0.016	0.003	-0.002	0.029	0.014	0.004
p_xC_{10}	0.137	-0.222	0.169	0.077	-0.058	-0.002
p_yC_{10}	0.116	0.242	0.155	0.276	-0.028	0.037
p_zC_{10}	-0.022	-0.139	-0.190	0.187	0.148	-0.048
sC_{11}	0.009	0.022	0.016	0.031	0.006	0.023
p_xC_{11}	0.233	-0.029	-0.029	-0.025		0.010
p_yC_{11}	0.104	0.028	0.009	0.015	0.035	0.024
p_zC_{11}	-0.043	-0.009	-0.021	0.019	-0.026	0.046
sC_{12}	-0.087	0.003	0.001	0.014	-0.024	0.011
p_xC_{12}	-0.233	0.054	0.091	0.041	0.082	-0.011
p_yC_{12}	0.027	-0.024	-0.117	0.025	-0.227	-0.041
p_zC_{12}	0.104	-0.002	0.008	-0.040	0.085	-0.070
sC_{13}	0.020	-0.004	0.005	-0.001	0.011	0.022
p_xC_{13}	0.132	-0.045	0.079	-0.099	0.208	0.026
p_yC_{13}	-0.009	0.021	0.152	-0.036	0.335	0.175
p_zC_{13}	-0.009	0.004	-0.086	0.066	-0.152	0.199
sC_{14}		0.021	-0.022	0.002	0.030	0.049
p_xC_{14}	-0.059	0.159	-0.204	-0.028	-0.115	-0.044
p_yC_{14}	-0.067	-0.058	-0.109	0.098	-0.376	-0.079
p_zC_{14}	0.020	-0.003	0.112	-0.062	0.055	-0.317

Table II (contd.)

sC_{15}	0.002	-0.020	-0.010	0.006	-0.026	0.013
p_xC_{15}	-0.022	-0.096	0.015	0.055	-0.127	09.089
p_yC_{15}	0.018	0.004	0.046	-0.058	0.206	0.002
p_zC_{15}		-0.024	-0.043	0.023	-0.017	0.175
sC_{16}	0.005	0.010	-0.028	0.001	-0.029	-0.014
p_xC_{16}	0.012	0.061	-0.068	-0.024	0.005	-0.062
p_yC_{16}	-0.044	0.007	0.023	0.034	0.024	0.072
p_zC_{16}	0.007	-0.001	0.002		-0.041	-0.066
sC_{17}	-0.030	0.070	-0.014	0.010	-0.010	0.008
p_xC_{17}	-0.122	0.054	-0.062	0.085	-0.126	0.060
p_yC_{17}	0.061		-0.006	-0.053	0.019	-0.108
p_zC_{17}	0.018	-0.024	0.036	-0.024	0.062	-0.034
sC_{18}	0.006	-0.003	0.004	-0.008	0.006	-0.039
p_xC_{18}	-0.011	0.005	-0.031	0.033	-0.064	0.003
p_yC_{18}	0.009	-0.009	-0.030	0.001	-0.095	-0.109
p_zC_{18}	0.018	-0.007	0.049	-0.053	0.069	-0.216
sC_{19}		0.003	0.025	-0.040	-0.022	0.009
p_xC_{19}	-0.028	0.061	-0.067	0.013	0.043	-0.052
p_yC_{19}	-0.041	-0.062	-0.012	-0.122	0.006	0.012
p_zC_{19}	-0.007	0.050	0.159	-0.215	-0.135	0.014
sO_1	-0.001	0.004	-0.003	-0.003	0.007	0.003
p_xO_1	-0.612	0.019	0.252	0.111	0.115	0.080
p_yO_1	-0.242	-0.026	0.115	0.028	0.008	-0.010
p_zO_1	0.104	-0.072	-0.123	0.022	-0.102	0.089
$sH(C_1\alpha)$	0.005	0.022	0.106	-0.159	-0.114	0.101
$sH(C_2\beta)$	0.003	-0.022	0.068	-0.166	-0.099	0.142
$sH(C_3\alpha)$	-0.001	0.007	0.044	-0.181	-0.086	0.145
$sH(C_4\beta)$	0.007	-0.016	0.088	-0.185	-0.100	0.113
$sH(C_5\alpha)$	-0.003	-0.001	0.114	-0.248	-0.117	0.050
$sH(C_6\beta)$	-0.005	0.027	0.083	-0.133	-0.074	-0.053
$sH(C_7\alpha)$	-0.014	0.005	0.080	-0.068	-0.065	-0.171
$sH(C_8\beta)$	-0.023	0.037	0.117	-0.069	-0.056	-0.295
$sH(C_9\alpha)$	-0.065	0.017	0.158	-0.071	-0.039	-0.111
$sH(C_{12}\beta)$	0.095	-0.003	0.065	-0.032	0.155	0.067
$sH(C_{14}\alpha)$	0.005	0.018	0.079	-0.053	0.003	-0.338
$sH(C_{15}\beta)$	0.005	0.013	0.049	-0.026	0.013	-0.183
$sH(C_{16}\alpha)$	-0.027	-0.012	0.018	0.033	-0.049	
$sH(C_{17}\beta)$	0.038	-0.016	0.030	-0.022	0.065	0.043
$sH(C_{15}\alpha)$	0.017	0.027	0.021	-0.028	0.143	0.124
$sH(C_{16}\beta)$	-0.019	0.034	0.023	0.023	0.007	0.098
$sH(C_{17}\alpha)$	0.005	-0.015	0.035	-0.025	0.074	-0.036
$sH(C_1\beta)$	0.066	0.091	0.131	0.238	-0.042	-0.032
$sH(C_2\alpha)$	-0.009	-0.205	-0.089	0.056	0.102	-0.096
$sH(C_3\beta)$	-0.034	0.130	-0.162	-0.018	0.104	-0.060
$sH(C_4\alpha)$	0.061	0.074	0.114	0.231	-0.041	-0.038
$sH(C_6\alpha)$	0.080	0.058	0.114	0.116	0.093	0.098
$sH(C_7\beta)$	-0.049	-0.186	-0.020	0.075	-0.016	0.046
$sH(C_{12}\alpha)$	0.076	-0.009	-0.024	-0.030	0.003	-0.094
$sH(C_{18})$	0.011	0.001	0.058	-0.033	0.146	0.068
$sH(C_{18})$	-0.027	0.013	-0.036	0.049	-0.062	0.086
$sH(C_{18})$	0.006	-0.009	-0.044	0.016	-0.097	0.024
$sH(C_{19})$	0.049	0.060	0.057	0.117	-0.025	0.008
$sH(C_{19})$	-0.042	0.054	-0.107	0.017	0.065	-0.042
$sH(C_{19})$	-0.002	-0.124	-0.061	0.047	0.057	0.018

sC_{15}	0.003	0.020	-0.038	0.010	-0.005	-0.042
p_xC_{15}	0.011	0.090	-0.162	0.078	0.164	0.075
p_yC_{15}	-0.013	-0.126	0.117	-0.012	-0.124	0.029
p_zC_{15}	0.006	0.057	-0.081	0.094	-0.080	-0.184
sC_{16}		0.025	0.006	-0.011	-0.002	-0.048
p_xC_{16}	-0.004	0.011	0.077	-0.053	-0.108	-0.178
p_yC_{16}	-0.003		0.082	0.072	0.024	0.185
p_zC_{16}	0.001	-0.003	-0.006	-0.011	0.090	0.073
sC_{17}	-0.002	0.029	0.046	0.013	0.016	0.020
p_xC_{17}	-0.006	0.184	0.177	0.090	0.184	0.223
p_yC_{17}		-0.031	-0.054	-0.094	-0.059	-0.179
p_zC_{17}		-0.029	-0.013	-0.054	-0.096	-0.034
sC_{18}		-0.011	-0.007	-0.039	-0.019	-0.006
p_xC_{18}		0.056	0.048	0.077	0.104	0.122
p_yC_{18}	0.002	0.041	-0.048	-0.096	0.041	-0.097
p_zC_{18}	-0.001	-0.071	-0.009	-0.205	-0.089	0.049
sC_{19}	0.001	-0.004	-0.006	-0.026	0.005	-0.007
p_xC_{19}	-0.001	0.038	0.078	0.006	-0.045	
p_yC_{19}	0.012	0.026	-0.038	-0.073	-0.099	0.047
p_zC_{19}	-0.008	-0.026	-0.008	-0.170	0.077	-0.054
sO_1		-0.002	-0.005	0.001	0.003	0.004
p_xO_1	0.025	0.009	0.026	0.014	-0.020	-0.008
p_yO_1	-0.655	0.074	-0.156		-0.111	0.128
p_zO_1	0.277	-0.077	-0.028	-0.004	0.118	-0.004
$sH(C_1\alpha)$	0.020	-0.025	0.006	-0.064	0.064	-0.061
$sH(C_1\beta)$	-0.140	-0.056	0.012	0.026	0.113	-0.033
$sH(C_2\beta)$	0.075	-0.026	0.009	-0.022	0.063	-0.047
$sH(C_2\alpha)$	0.105	0.006	-0.081	0.029	-0.054	0.094
$sH(C_5\alpha)$	-0.028		-0.042	-0.093	-0.016	0.035
$sH(C_4\beta)$	-0.074		-0.052	-0.029	-0.018	0.045
$sH(C_4\alpha)$	-0.104	-0.058	-0.035	0.035	0.115	-0.040
$sH(C_6\beta)$	-0.016	0.011	-0.009	-0.090	0.020	0.019
$sH(C_7\alpha)$	-0.004	0.003		-0.148	0.086	0.024
$sH(C_8\beta)$	-0.003	-0.034		-0.295	0.134	0.064
$sH(C_9\alpha)$	-0.003	-0.022	-0.024	-0.279	0.038	-0.004
$sH(C_{11}\beta)$	0.004	-0.007	-0.053	-0.201	-0.068	-0.024
$sH(C_{12}\alpha)$		-0.035	-0.033	-0.162	-0.091	-0.002
$sH(C_{14}\alpha)$		-0.052	0.005	-0.248	0.117	0.141
$sH(C_{15}\beta)$	-0.001	-0.026	0.025	-0.092	0.118	0.171
$sH(C_{16}\alpha)$		0.018	0.020	0.042	0.134	0.196
$sH(C_{17}\beta)$	0.002	-0.070	-0.038	0.049	-0.017	
$sH(C_{15}\alpha)$	-0.007	-0.096	0.040	0.041	-0.143	-0.050
$sH(C_{16}\beta)$	0.002	0.021	-0.039	0.050	0.006	0.047
$sH(C_{17}\alpha)$		-0.064	-0.021	-0.069	-0.138	-0.058
$sH(C_6\alpha)$	-0.029	-0.167	0.008	0.099	0.112	-0.063
$sH(C_7\beta)$	0.062	0.072	-0.164	0.051	-0.056	0.086
$sH(C_{11}\alpha)$	0.025	0.104	-0.164	0.095	-0.013	-0.139
$sH(C_{12}\beta)$	-0.010	-0.201	0.020	0.115	-0.030	0.070
$sH(C_{18})$	-0.003	-0.099	0.018	0.029	-0.116	0.031
$sH(C_{18})$	-0.001	0.076	0.063	0.110	0.124	0.137
$sH(C_{18})$	0.004	0.055	-0.060	0.029	0.038	-0.167
$sH(C_{19})$	-0.021	-0.052	0.019	0.049	0.134	-0.066
$sH(C_{19})$	0.003	0.059	0.091	0.017	-0.085	0.013
$sH(C_{19})$	0.018	0.008	-0.077	0.067	-0.072	0.072

sC_{15}	-0.018	-0.029	0.011	0.022	0.029	-0.033
p_xC_{15}	-0.062	-0.145	0.054	0.139	0.008	0.098
p_yC_{15}	0.101	0.088	-0.020	-0.154	0.005	0.016
p_zC_{15}	-0.053	-0.060	0.090	0.045	0.162	-0.083
sC_{16}	-0.023	0.008	-0.006	0.019	0.008	-0.036
p_xC_{16}	-0.021	0.061	-0.035	-0.031	0.034	-0.162
p_yC_{16}	-0.003	0.052	0.050	-0.028	-0.064	0.187
p_zC_{16}	-0.003	-0.002	-0.023	0.029	-0.039	0.035
sC_{17}	-0.026	0.038	0.011	0.007	-0.017	0.037
p_xC_{17}	-0.151	0.139	0.078	0.110	-0.135	0.303
p_yC_{17}	0.025	-0.031	-0.072	-0.006	0.039	-0.201
p_zC_{17}	0.011	-0.004	-0.021	-0.032	-0.024	-0.053
sC_{18}	0.007	-0.005	-0.027	-0.008	-0.022	-0.031
p_xC_{18}	-0.046	0.035	0.072	0.055	-0.043	0.156
p_yC_{18}	-0.035	-0.025	-0.064	0.076	-0.043	-0.108
p_zC_{18}	0.051	-0.009	-0.148	-0.063	-0.147	-0.099
sC_{19}	0.003	-0.005	-0.038	0.004	0.034	0.020
p_xC_{19}	-0.043	0.070	0.028	-0.043	-0.062	-0.046
p_yC_{19}	-0.043	-0.048	-0.101	-0.072	0.078	0.057
p_zC_{19}	0.029	0.007	-0.227	0.061	0.159	0.102
$sH(C_1\alpha)$	0.020	-0.005	-0.111	0.031	0.148	0.099
$sH(C_2\beta)$	0.018	-0.015	-0.067	0.028	0.151	0.111
$sH(C_3\alpha)$	0.009	-0.005	-0.058	0.015	0.166	0.117
$sH(C_4\beta)$	0.020	-0.030	-0.083	0.023	0.185	0.152
$sH(C_5\alpha)$	0.008	-0.025	-0.154	0.019	0.219	0.170
$sH(C_6\beta)$	-0.008	0.010	-0.112	0.034	0.096	0.076
$sH(C_7\alpha)$	0.005	0.019	-0.141	0.055	-0.035	0.021
$sH(C_8\beta)$	0.042	0.007	-0.279	0.054	-0.159	-0.004
$sH(C_9\alpha)$	0.015	-0.017	-0.303	0.031	-0.028	-0.002
$sH(C_{11}\beta)$	-0.059	-0.054	-0.200	-0.009	-0.021	-0.092
$sH(C_{12}\alpha)$	0.023	-0.032	-0.133	-0.032	-0.063	-0.106
$sH(C_{14}\alpha)$	0.051	0.003	-0.210	0.013	-0.239	-0.007
$sH(C_{15}\beta)$	0.031	0.011	-0.083	0.005	-0.153	0.082
$sH(C_{16}\alpha)$	-0.015	0.006	0.026	0.041	-0.082	0.197
$sH(C_{17}\beta)$	0.061	-0.036	0.023	-0.048	0.066	0.002
$sH(C_{15}\alpha)$	0.073	0.030	0.031	-0.119	0.096	-0.035
$sH(C_{16}\beta)$	-0.008	-0.027	0.041	0.009	0.023	0.039
$sH(C_{17}\alpha)$	0.043	-0.017	-0.041	-0.067	-0.004	-0.115
$sH(C_1\beta)$	0.123	0.054	0.049	0.185	-0.088	-0.036
$sH(C_2\alpha)$	-0.047	-0.151	0.049	-0.120	-0.134	0.004
$sH(C_3\beta)$	-0.071	0.125	0.016	-0.087	0.010	-0.131
$sH(C_4\alpha)$	0.120	0.022	0.064	0.190	-0.094	-0.087
$sH(C_6\alpha)$	0.186	0.025	0.094	0.049	-0.007	-0.027
$sH(C_7\beta)$	-0.079	-0.191	0.049	-0.011	-0.051	0.018
$sH(C_{11}\alpha)$	-0.101	-0.122	0.097	0.065	0.145	-0.116
$sH(C_{12}\beta)$	0.180	-0.001	0.092	-0.109	0.035	0.078
$sH(C_{18})$	0.082	0.001	0.010	-0.121	0.055	0.003
$sH(C_{18})$	-0.058	0.046	0.088	0.060	-0.038	0.192
$sH(C_{18})$	-0.046	-0.033	0.025	0.079	0.093	-0.086
$sH(C_{19})$	0.076	0.037	0.065	0.107	-0.043	-0.040
$sH(C_{19})$	-0.068	0.076	0.039	-0.075	-0.053	-0.041
$sH(C_{19})$	-0.018	-0.090	0.078	-0.055	-0.043	-0.010

Table II (contd.)

5α-Androstan-17-one

ε_i/eV	-10.367	-11.210	-11.313	-11.698	-11.819	-11.948
sC_1	-0.001	-0.050	-0.008	-0.029	0.016	-0.006
p_xC_1	-0.016	0.031	0.235	-0.025	0.033	0.041
p_yC_1	0.005	-0.203	-0.046	-0.019	0.148	0.090
p_zC_1	-0.004	0.170	0.107	0.154	-0.054	0.123
sC_2	-0.003	0.010	0.020	-0.006	-0.013	-0.011
p_xC_2	0.020	0.031	-0.225	0.054	-0.075	-0.039
p_yC_2	0.001	0.130	-0.002	0.015	-0.184	-0.102
p_zC_2	0.002	-0.082	-0.056	-0.094	-0.065	-0.143
sC_3	0.001	0.001	-0.020	-0.006	-0.004	-0.031
p_xC_3	-0.012	-0.018	0.182	-0.041	0.025	0.046
p_yC_3	0.001	-0.151	-0.029	-0.022	0.212	0.082
p_zC_3	-0.002	0.078	0.053	0.079	-0.077	0.171
sC_4	-0.007	-0.023	0.027	-0.020	0.010	-0.024
p_xC_4	0.036	0.041	-0.287	0.072	0.012	0.022
p_yC_4	0.002	0.140	0.021	-0.005	-0.194	-0.075
p_zC_4	0.002	-0.056	-0.060	-0.098	0.042	-0.207
sC_5	0.003	0.020	-0.009	-0.028	-0.018	-0.026
p_xC_5	-0.032	-0.072	0.284	-0.052	0.031	0.004
p_yC_5	-0.021	-0.311	0.028	0.079	0.216	0.087
p_zC_5	0.003	0.092	0.063	0.159	-0.017	0.246
sC_6	-0.010	-0.036	-0.001	-0.018	0.014	-0.023
p_xC_6	0.050	-0.011	-0.204	-0.019	0.117	-0.019
p_yC_6	0.014	0.202	0.039	-0.047	-0.081	0.058
p_zC_6	-0.002	-0.105	-0.081	-0.137	0.064	-0.140
sC_7	0.009	0.026	0.023	-0.036	0.022	0.017
p_xC_7	-0.054	-0.051	0.194	0.033	-0.119	-0.038
p_yC_7	-0.044	-0.187	-0.031	0.145	-0.125	-0.114
p_zC_7	0.006	0.078	0.056	0.102	0.020	-0.016
sC_8	-0.016	-0.012	-0.024	-0.033	-0.022	0.032
p_xC_8	0.120	0.018	-0.191	-0.006	0.066	0.026
p_yC_8	0.012	0.226	0.075	-0.129	0.148	0.088
p_zC_8	-0.018	-0.131	-0.097	-0.213	-0.115	0.189
sC_9	-0.009	-0.015	0.028	-0.052	0.002	0.014
p_xC_9	-0.055	-0.051	0.360	-0.053	0.044	-0.064
p_yC_9	-0.002	-0.232	-0.071	0.159	-0.123	-0.028
p_zC_9	0.016	0.126	0.046	0.231	0.117	-0.126
sC_{10}	-0.011	0.009	0.008	-0.030	-0.004	-0.017
p_xC_{10}	0.073	0.049	-0.348	0.085	-0.042	-0.021
p_yC_{10}	0.010	0.308	-0.002	-0.110	-0.226	-0.116
p_zC_{10}	-0.011	-0.156	-0.058	-0.268	0.048	-0.153
sC_{11}	-0.023	0.036	-0.013	-0.021	0.002	0.005
p_xC_{11}	0.133	0.059	-0.109	-0.029	-0.039	0.063
p_yC_{11}	-0.016	0.221	-0.054	-0.148	0.073	0.044
p_zC_{11}	0.002	-0.085	0.005	-0.111	-0.123	0.125
sC_{12}	0.002	-0.017	0.031	-0.007	-0.029	0.005
p_xC_{12}	-0.111	0.002	0.118	-0.008	0.088	-0.067
p_yC_{12}	0.029	-0.139	0.052	0.093	-0.197	-0.049
p_zC_{12}	-0.014	0.067	-0.015	0.052	0.183	-0.119
sC_{13}	-0.061	0.009	-0.031	-0.008	0.010	0.025
p_xC_{13}	0.401	-0.007	0.040	-0.052	0.015	0.059
p_yC_{13}	-0.032	0.172	-0.058	-0.115	0.294	0.103
p_zC_{13}	-0.088	-0.076	-0.018	-0.043	-0.189	0.159
sC_{14}	-0.007	0.006	0.031	-0.032	0.006	0.025
p_xC_{14}	-0.093	-0.032	0.209	-0.033	-0.072	-0.033
p_yC_{14}	-0.117	-0.137	-0.016	0.113	-0.260	-0.085
p_zC_{14}	0.059	0.066	0.009	0.097	0.150	-0.188

5α-Androstane-3,17-dione

ε_i/eV	-10.453	-10.601	-11.511	-11.721	-11.906	-12.188
sC_1	0.002	0.028	-0.030	-0.025	-0.019	-0.035
p_xC_1	-0.006	0.054	0.046	0.193	-0.022	0.043
p_yC_1	0.011	0.111	-0.119	-0.066	-0.011	-0.155
p_zC_1	-0.005	-0.032	0.122	0.123	0.100	0.171
sC_2	-0.007	-0.083	-0.017	0.021	-0.011	-0.019
p_xC_2	0.006	-0.123	-0.020	-0.193	0.045	-0.005
p_yC_2	-0.019	-0.349	-0.036	-0.012	-0.009	-0.010
p_zC_2	0.002	0.005	-0.045	-0.051	-0.039	-0.094
sC_3	0.001	-0.001	0.002	-0.022	0.001	0.001
p_xC_3	-0.003	-0.007	-0.009	0.065	-0.023	-0.006
p_yC_3	0.013	0.238	0.008	0.007	0.004	-0.024
p_zC_3	-0.007	-0.112	-0.003	-0.004	0.015	0.011
sC_4	-0.002	0.085	0.002	0.053	-0.017	0.014
p_xC_4	0.032	0.126	0.086	-0.218	0.087	0.048
p_yC_4	-0.008	-0.221	0.020	-0.049	-0.016	-0.094
p_zC_4	0.013	0.265	0.053	0.027	-0.035	0.084
sC_5	0.002	-0.019	0.016	-0.027	-0.018	0.024
p_xC_5	-0.024	-0.065	-0.086	0.220	-0.060	-0.069
p_yC_5	-0.011	0.098	0.236	0.045	0.064	-0.328
p_zC_5	-0.001	-0.070	0.031	0.046	0.100	-0.016
sC_6	-0.008	0.032	-0.018	0.013	-0.017	-0.008
p_xC_6	0.046	0.079	0.057	0.178	0.032	-0.075
p_yC_6	0.008	-0.090	0.157	0.008	-0.050	0.141
p_zC_6		0.081	-0.032	-0.049	-0.095	-0.046
sC_7	0.008	-0.014	0.031	0.016	-0.037	-0.023
p_xC_7	-0.048	-0.049	-0.104	0.183	-0.003	0.081
p_yC_7	-0.040	0.037	-0.229	-0.032	0.134	0.067
p_zC_7	0.003	-0.017	0.061	0.068	0.112	0.060
sC_8	-0.017	0.003	-0.016	-0.028	-0.042	0.008
p_xC_8	0.113	0.007	0.046	-0.234	0.041	-0.059
p_yC_8	0.011	-0.032	0.276	0.100	-0.109	-0.054
p_zC_8	-0.017	0.018	-0.131	-0.136	-0.271	-0.045
sC_9	-0.007	0.004	-0.013	0.014	-0.052	-0.016
p_xC_9	-0.042	-0.005	-0.051	0.381	-0.072	-0.047
p_yC_9	-0.002	0.029	-0.281	-0.097	0.120	-0.002
p_zC_9	0.014	-0.020	0.128	0.083	0.271	0.004
sC_{10}	-0.011	0.002	0.010	0.016	-0.029	0.009
p_xC_{10}	0.062	0.007	0.054	-0.370	0.128	0.058
p_yC_{10}	0.003	-0.079	0.233	-0.007	-0.094	0.340
p_zC_{10}	-0.008	0.046	-0.090	-0.062	-0.215	-0.120
sC_{11}	-0.025	-0.002	0.038	-0.009	-0.017	0.016
p_xC_{11}	0.129	-0.008	0.053	-0.142	-0.022	0.067
p_yC_{11}	-0.020	-0.025	0.258	-0.038	-0.115	0.027
p_zC_{11}	0.003	0.011	-0.090	-0.031	-0.163	0.090
sC_{12}	0.004	-0.001	-0.025	0.031	-0.017	0.029
p_xC_{12}	-0.108	0.001	0.023	0.157	-0.002	-0.098
p_yC_{12}	0.031	0.006	-0.209	0.049	0.054	0.177
p_zC_{12}	-0.013	-0.002	0.095	0.011	0.111	-0.184
sC_{13}	-0.062	0.005	0.014	-0.036	-0.007	-0.012
p_xC_{13}	0.404	-0.022	0.001	0.019	-0.061	-0.029
p_yC_{13}	-0.025	-0.007	0.269	-0.048	-0.075	-0.314
p_zC_{13}	-0.088	0.011	-0.103	-0.052	-0.111	0.155
sC_{14}	-0.004	-0.004	0.008	0.025	-0.040	-0.020
p_xC_{14}	-0.083	-0.009	-0.061	0.246	-0.079	0.052
p_yC_{14}	-0.118	0.014	-0.225	-0.026	0.079	0.278
p_zC_{14}	0.048	-0.003	0.089	0.040	0.175	-0.050

5α-Androstane-3,11,17-trione

ε_i/eV	-10.474	-10.618	-11.059	-11.919	-12.085	-12.243
sC_1	0.005	0.023	0.002	-0.050	0.029	0.010
p_xC_1	0.036	0.049	-0.009	0.222	0.075	-0.025
p_yC_1	0.066	0.107	-0.040	-0.153	0.052	-0.072
p_zC_1	-0.013	-0.023	0.013	0.248	-0.144	-0.125
sC_2	-0.014	-0.080	-0.021	0.005	0.024	-0.003
p_xC_2	-0.064	-0.116	0.009	-0.189	-0.110	0.018
p_yC_2	-0.094	-0.331	-0.051	-0.015	0.013	0.021
p_zC_2	0.001	0.003	-0.004	-0.117	0.078	0.074
sC_3	-0.005	-0.002	0.004	-0.022	-0.009	0.023
p_xC_3	0.006	-0.004	-0.008	0.059	0.066	-0.007
p_yC_3	0.072	0.229	0.025	-0.006	-0.002	-0.023
p_zC_3	-0.029	-0.102	-0.013	0.006	-0.037	-0.040
sC_4	0.034	0.078	0.006	0.043	0.037	0.004
p_xC_4	-0.011	0.137	0.063	-0.124	-0.218	-0.001
p_yC_4	-0.075	-0.218	-0.013	-0.004	-0.022	0.079
p_zC_4	0.066	0.244	0.047	0.052	0.038	0.101
sC_5	-0.024	-0.014	0.020	-0.012	0.003	0.032
p_xC_5	0.033	-0.074	-0.066	0.126	0.201	-0.036
p_yC_5	0.106	0.074	-0.101	-0.170	0.092	-0.203
p_zC_5	-0.020	-0.058	-0.100	0.083	-0.107	-0.211
sC_6	0.018	0.027	0.005	-0.010	0.037	0.001
p_xC_6	-0.014	0.088	0.001	-0.136	-0.171	0.108
p_yC_6	-0.057	-0.076	0.030	0.152	-0.083	0.123
p_zC_6	0.026	0.070	0.010	-0.096	0.089	0.151
sC_7	-0.024	-0.006	0.011	0.021	0.023	0.021
p_xC_7	0.044	-0.069	-0.023	0.106	0.183	-0.106
p_yC_7	0.096	0.002	-0.060	-0.132	0.015	-0.131
p_zC_7	-0.014	-0.009	0.005	0.096	-0.064	-0.085
sC_8	0.020	-0.006	0.008	-0.020	0.006	0.024
p_xC_8	-0.076	0.043	-0.052	-0.141	-0.201	0.109
p_yC_8	-0.080	-0.003	0.086	0.202	-0.013	0.127
p_zC_8	0.037	-0.001	0.006	-0.158	0.129	0.093
sC_9	-0.043	0.011	0.050	-0.010	0.080	-0.018
p_xC_9	0.137	-0.039	-0.140	0.273	0.193	0.028
p_yC_9	0.205	-0.023	-0.237	-0.167	-0.105	0.011
p_zC_9	-0.006	-0.009	-0.019	0.125	-0.167	-0.059
sC_{10}	0.015	-0.001	-0.005	0.007	0.008	0.034
p_xC_{10}	-0.092	0.034	0.074	-0.246	-0.222	0.045
p_yC_{10}	-0.076	-0.063	0.083	0.209	-0.078	0.241
p_zC_{10}	0.026	0.037	-0.002	-0.191	0.228	0.223
sC_{11}	0.014	-0.013	0.034	0.021	-0.020	0.039
p_xC_{11}	-0.188	0.042	0.128	-0.026	0.001	-0.010
p_yC_{11}	-0.061	0.005	0.092	0.034	-0.021	0.054
p_zC_{11}	0.017	0.001	-0.017	-0.027	0.045	0.002
sC_{12}	0.050	-0.004	-0.081	0.001	0.016	-0.003
p_xC_{12}	0.256	-0.051	-0.233	0.069	-0.041	0.085
p_yC_{12}	-0.034	0.012	-0.019	-0.054	0.127	-0.164
p_zC_{12}	-0.025	0.001	0.055	0.026	-0.052	0.035
sC_{13}	0.029	-0.017	0.073	-0.008	-0.023	0.016
p_xC_{13}	-0.294	0.120	-0.232	0.016		0.058
p_yC_{13}	0.039	-0.014	0.034	0.066	-0.164	0.250
p_zC_{13}	0.050	-0.028	0.104	-0.043	0.068	-0.040
sC_{14}	0.002	-0.005	0.003	0.022	0.032	0.016
p_xC_{14}	0.067	-0.040	0.025	0.145	0.230	-0.089
p_yC_{14}	0.093	-0.033	0.044	-0.123	0.084	-0.203

Table II (contd.)

p_zC_{14}	-0.035	0.018	-0.037	0.052	-0.120	-0.010
sC_{15}	0.007	-0.002	0.007	-0.026	0.015	-0.017
p_xC_{15}	-0.028	0.019	-0.053	-0.130	-0.026	-0.018
p_yC_{15}	-0.050	0.015	-0.044	0.123	-0.037	0.108
p_zC_{15}	0.013	-0.004	0.012	-0.059	0.066	-0.013
sC_{16}	-0.053	0.021	-0.048	0.009	0.034	-0.021
p_xC_{16}		-0.004	0.010	0.076	0.087	-0.040
p_yC_{16}	0.245	-0.104	0.244	-0.001	-0.062	0.032
p_zC_{16}	-0.067	0.029	-0.068	0.004	-0.004	-0.013
sC_{17}	0.025	-0.007	-0.021	0.024	0.023	-0.001
p_xC_{17}	0.145	-0.055	0.071	0.014	0.015	-0.003
p_yC_{17}	-0.149	0.060	-0.127	0.014	0.028	-0.015
p_zC_{17}	0.014	-0.006	0.015	-0.005	-0.009	0.002
sC_{18}	-0.018	0.008	-0.017	0.001	-0.001	-0.007
p_xC_{18}	0.041	-0.019	0.054	-0.011	0.012	-0.015
p_yC_{18}	-0.028	0.012	-0.026	-0.017	0.040	-0.089
p_zC_{18}	-0.056	0.025	-0.065	0.018	-0.037	-0.015
sC_{19}	0.001	0.001	-0.004	0.009	-0.034	-0.045
p_xC_{19}	0.015	-0.006	-0.014	0.073	0.101	0.008
p_yC_{19}	0.021	0.005	-0.033	-0.055	-0.014	-0.129
p_zC_{19}	0.002	-0.006	-0.021	0.094	-0.207	-0.243
sO_1			0.001	-0.008	-0.005	0.006
p_xO_1	0.007	0.007	-0.003	0.028	0.093	0.074
p_yO_1	-0.177	-0.624	-0.107	-0.216	-0.012	-0.020
p_zO_1	0.060	0.286	0.069	-0.026	-0.153	-0.010
sO_2	0.002	-0.001	-0.002	0.001	0.005	-0.004
p_xO_2	-0.285	0.124	-0.306	0.014	0.037	0.010
p_yO_2	0.355	-0.155	0.397	-0.017	-0.085	0.022
p_zO_2	-0.033	0.018	-0.080	0.008	0.026	-0.022
sO_3	0.002	0.002	0.003	0.008		0.004
p_xO_3	0.436	-0.069	-0.484	0.055	-0.168	0.213
p_yO_3	0.161	-0.017	-0.224	-0.049	-0.005	0.032
p_zO_3	-0.039	0.015	0.039	-0.073	0.129	0.002
$sH(C_1\alpha)$	0.005	0.020	0.001	0.077	-0.140	-0.144
$sH(C_1\beta)$	-0.070	-0.126	0.031	0.030	-0.046	0.114
$sH(C_2\beta)$	0.017	0.074	0.017	0.046	-0.100	-0.075
$sH(C_2\alpha)$	0.026	0.102	0.012	-0.156	0.046	0.058
$sH(C_5\alpha)$	-0.008	-0.029	-0.020	-0.015	-0.138	-0.266
$sH(C_4\beta)$	-0.020	-0.068	-0.017	-0.060	-0.085	-0.130
$sH(C_4\alpha)$	-0.056	-0.094	0.024	0.001	-0.060	0.111
$sH(C_6\beta)$	0.001	-0.018	-0.017	0.024	-0.076	-0.181
$sH(C_7\alpha)$	0.002	-0.004	-0.014	0.041	-0.078	-0.123
$sH(C_8\beta)$	0.001	0.002	-0.037	0.056	-0.151	-0.115
$sH(C_9\alpha)$	0.042	-0.009	-0.077	0.039	-0.181	-0.095
$sH(C_{12}\beta)$	-0.062	0.013	0.064	0.020	-0.084	0.115
$sH(C_{14}\alpha)$	-0.021	0.011	-0.034	0.037	-0.106	-0.055
$sH(C_{15}\beta)$	-0.021	0.009	-0.024	0.024	-0.069	-0.003
$sH(C_{16}\beta)$	0.053	-0.020	0.046	-0.049	-0.029	0.022
$sH(C_6\alpha)$	-0.058	-0.004	0.045	0.066	-0.118	0.207
$sH(C_7\beta)$	0.045	0.043	-0.033	-0.207	-0.001	0.041
$sH(C_{12}\alpha)$	-0.072	0.017	0.036	-0.005	0.009	-0.045
$sH(C_{15}\alpha)$	-0.059	0.021	-0.055	0.051	-0.005	0.090
$sH(C_{16}\alpha)$	0.061	-0.024	0.055	-0.022	-0.048	0.007
$sH(C_{18})$	-0.028	0.012	-0.031	0.025	-0.047	0.089
$sH(C_{18})$	0.076	-0.033	0.082	-0.007	0.001	0.012
$sH(C_{18})$	-0.009	0.003	-0.001	-0.025	0.058	-0.060
$sH(C_{19})$	-0.028	-0.009	0.035	0.047	-0.057	0.104
$sH(C_{19})$	0.023	-0.007	-0.019	0.073	0.136	0.021
$sH(C_{19})$	0.004	0.017	0.001	-0.152	0.073	0.081

sC_{15}	-0.008	0.003	-0.035	-0.020	-0.010	0.028
p_xC_{15}	0.050	0.005	-0.105	-0.130	-0.012	0.082
p_yC_{15}	0.068	-0.014	0.135	0.082	-0.021	-0.158
p_zC_{15}	-0.013	0.005	-0.083	-0.048	-0.084	0.058
sC_{16}	0.074	-0.004	-0.025	0.030	-0.009	0.025
p_xC_{16}	0.012	-0.004	-0.008	0.113	-0.015	0.024
p_yC_{16}	-0.354	0.018	0.073	-0.051	0.027	-0.052
p_zC_{16}	0.090	-0.005	-0.006	0.015	0.017	0.012
sC_{17}	-0.019	-0.001	-0.003	0.042	-0.013	0.001
p_xC_{17}	-0.192	0.008	0.002	0.024	-0.006	0.006
p_yC_{17}	0.194	-0.011	-0.022	0.040	-0.005	0.014
p_zC_{17}	-0.023	0.002	0.005	-0.003	0.014	-0.016
sC_{18}	0.025	-0.001	-0.001	0.008	0.017	-0.007
p_xC_{18}	-0.072	0.004	0.001	-0.015	-0.027	0.016
p_yC_{18}	0.037	-0.001	-0.062	0.017	0.051	0.108
p_zC_{18}	0.085	-0.006	0.026	0.039	0.119	-0.080
sC_{19}	0.002				0.038	-0.004
p_xC_{19}	-0.009		-0.015	0.105	-0.045	-0.016
p_yC_{19}	0.005	0.008	-0.060	-0.001	0.093	-0.146
p_zC_{19}	0.008	-0.009	0.020	0.025	0.229	0.041
sO_1			0.001	-0.007	0.001	0.001
p_xO_1	-0.003	0.020	-0.006	0.059	-0.048	0.003
p_yO_1	-0.031	-0.645	-0.129	-0.126	0.009	-0.147
p_zO_1	0.024	0.304	0.083	-0.089	0.056	0.084
sO_2	-0.002		-0.004	0.005		0.006
p_xO_2	0.451	-0.026	-0.035	0.073	-0.039	-0.007
p_yO_2	-0.502	-0.029	0.086	-0.104	0.059	-0.060
p_zO_2	0.073	-0.006	-0.020	0.049	0.026	-0.009
$sH(C_1\alpha)$	0.005	0.020	0.033	0.008	0.104	0.063
$sH(C_1\beta)$	-0.006	-0.136	0.081	-0.033	-0.011	0.120
$sH(C_2\beta)$	0.006	0.072	0.037	-0.005	0.050	0.069
$sH(C_2\alpha)$	0.010	0.106	-0.045	-0.092	-0.025	-0.095
$sH(C_5\alpha)$	0.004	-0.034	-0.027	-0.015	0.149	-0.103
$sH(C_4\beta)$		-0.072	-0.026	-0.049	0.064	-0.087
$sH(C_4\alpha)$	0.003	-0.105	0.067	-0.082	-0.010	0.140
$sH(C_6\beta)$		-0.019	-0.021	0.025	0.117	-0.021
$sH(C_7\alpha)$	0.001	-0.005	-0.002	0.038	0.164	0.054
$sH(C_8\beta)$	0.017	-0.003	0.028	0.041	0.303	0.057
$sH(C_9\alpha)$	0.014	-0.004	-0.002	0.023	0.315	-0.007
$sH(C_{11}\beta)$	0.029	0.002	-0.045	-0.003	0.213	-0.053
$sH(C_{12}\alpha)$	0.048	-0.002	-0.005	0.007	0.128	-0.069
$sH(C_{14}\alpha)$	0.035	-0.003	-0.052	0.032	0.207	0.002
$sH(C_{15}\beta)$	0.025	-0.002	0.043	0.012	0.090	-0.021
$sH(C_{16}\beta)$	-0.073	0.006	-0.007	-0.070	-0.012	-0.007
$sH(C_{15}\alpha)$	0.085	-0.010	0.069	0.030	-0.069	-0.110
$sH(C_{16}\alpha)$	-0.084	0.006	0.018	-0.041	0.029	-0.007
$sH(C_6\alpha)$	0.028	-0.025	0.181	-0.078	-0.070	0.102
$sH(C_7\beta)$	0.002	0.059	-0.139	-0.154	-0.031	-0.060
$sH(C_{11}\alpha)$	-0.039	0.018	-0.177	-0.070	-0.120	0.109
$sH(C_{12}\beta)$	0.025	-0.009	0.188	-0.089	-0.088	-0.100
$sH(C_{18})$	0.034	-0.004	0.071	-0.005	-0.026	-0.125
$sH(C_{18})$	-0.117	0.006	0.004	-0.022	-0.038	0.014
$sH(C_{18})$	0.022	0.001	-0.073	-0.006	-0.033	0.127
$sH(C_{19})$	0.002	-0.017	0.081	-0.031	-0.040	0.169
$sH(C_{19})$	-0.015	0.002	-0.031	0.124	-0.073	-0.048
$sH(C_{19})$	0.005	0.017	-0.045	-0.091	-0.072	-0.099

sC_{15}	-0.008	-0.025	-0.015	-0.001	-0.040	0.016
p_xC_{15}	0.051	-0.076	-0.084	0.003	-0.118	0.063
p_yC_{15}	0.065	0.088	0.062	-0.042	0.160	0.009
p_zC_{15}	-0.020	-0.062	-0.032	-0.038	-0.123	0.112
sC_{16}	0.073	-0.018	0.030	-0.001	-0.028	-0.005
p_xC_{16}	0.006	-0.001	0.083	-0.001	-0.011	-0.038
p_yC_{16}	-0.341	0.055	-0.064	0.010	0.070	-0.010
p_zC_{16}	0.124	-0.014	0.024	0.010	-0.009	-0.029
sC_{17}	-0.020	-0.001	0.033	-0.007	-0.002	-0.005
p_xC_{17}	-0.190	0.007	0.009	-0.001	-0.004	-0.008
p_yC_{17}	0.192	-0.018	0.041	0.001	-0.017	-0.014
p_zC_{17}	-0.040	0.005	-0.012	0.007	0.012	-0.017
sC_{18}	0.025	-0.001	0.005	0.011	0.008	-0.027
p_xC_{18}	-0.071	0.003	-0.014	-0.020	-0.015	0.013
p_yC_{18}	0.042	-0.036	0.016	0.056	-0.074	-0.077
p_zC_{18}	0.082	0.014	0.018	0.070	0.090	-0.151
sC_{19}	0.002	0.002	-0.002	0.046	0.009	0.033
p_xC_{19}	-0.012	-0.015	0.090	0.052	0.007	-0.070
p_yC_{19}	0.004	-0.068	-0.007	0.115	0.088	0.086
p_zC_{19}	0.010	0.046	0.011	0.269	0.016	0.135
sO_1	-0.002	-0.002	0.004	0.001	-0.005	-0.002
p_xO_1	0.442	-0.035	0.083	-0.026	-0.014	-0.004
p_yO_1	-0.497	0.068	-0.114	0.033	0.078	-0.018
p_zO_1	0.116	-0.023	0.050	0.018	-0.015	-0.059
$sH(C_1\alpha)$	0.005	0.032	-0.005	0.146	0.015	0.146
$sH(C_2\beta)$	0.003	0.021	-0.019	0.094	0.008	0.160
$sH(C_3\alpha)$	0.003	0.009	-0.020	0.079	0.020	0.181
$sH(C_4\beta)$	0.006	0.001	-0.036	0.117	0.043	0.223
$sH(C_5\alpha)$	0.008	-0.001	-0.014	0.207	0.053	0.259
$sH(C_6\beta)$	0.003	0.008	0.017	0.147	0.006	0.106
$sH(C_7\alpha)$	0.004	0.005	0.011	0.156	0.001	-0.057
$sH(C_8\beta)$	0.018	0.026	0.012	0.251	0.049	-0.119
$sH(C_9\alpha)$	0.016	-0.002	-0.004	0.297	0.054	-0.112
$sH(C_{11}\beta)$	0.030	-0.041	-0.012	0.179	0.034	-0.113
$sH(C_{12}\alpha)$	0.048	-0.006	-0.004	0.096	0.051	-0.121
$sH(C_{14}\alpha)$	0.037	0.035	0.008	0.138	0.088	-0.214
$sH(C_{15}\beta)$	0.032	0.028	0.002	0.050	0.069	-0.102
$sH(C_{16}\beta)$	-0.071	-0.004	-0.052	-0.009	-0.012	0.047
$sH(C_{15}\alpha)$	0.081	0.042	0.029	-0.062	0.080	0.073
$sH(C_{16}\alpha)$	-0.084	0.010	-0.039	0.014	0.019	-0.015
$sH(C_1\beta)$	0.004	0.175	-0.049	-0.007	-0.167	-0.119
$sH(C_2\alpha)$	0.007	-0.138	-0.121	-0.085	0.123	-0.103
$sH(C_3\beta)$	-0.015	-0.025	0.195	-0.063	0.026	-0.002
$sH(C_4\alpha)$	0.011	0.154	-0.068	-0.016	-0.191	-0.124
$sH(C_6\alpha)$	0.033	0.179	-0.067	-0.097	-0.019	0.007
$sH(C_7\beta)$	-0.001	-0.154	-0.138	-0.049	-0.027	-0.023
$sH(C_{11}\alpha)$	0.037	-0.138	-0.024	-0.071	-0.173	0.123
$sH(C_{12}\beta)$	0.029	0.136	-0.079	-0.108	-0.135	0.093
$sH(C_{18})$	0.037	0.041	-0.004	-0.034	0.099	0.042
$sH(C_{18})$	0.116	0.008	-0.021	-0.029	-0.011	0.031
$sH(C_{18})$	0.018	-0.045	0.007	-0.003	-0.118	0.050
$sH(C_{19})$	0.004	0.101	-0.023	-0.045	-0.097	-0.044
$sH(C_{19})$	-0.019	-0.036	0.110	-0.076	0.022	-0.059
$sH(C_{19})$	0.005	-0.070	-0.078	-0.096	0.034	-0.022

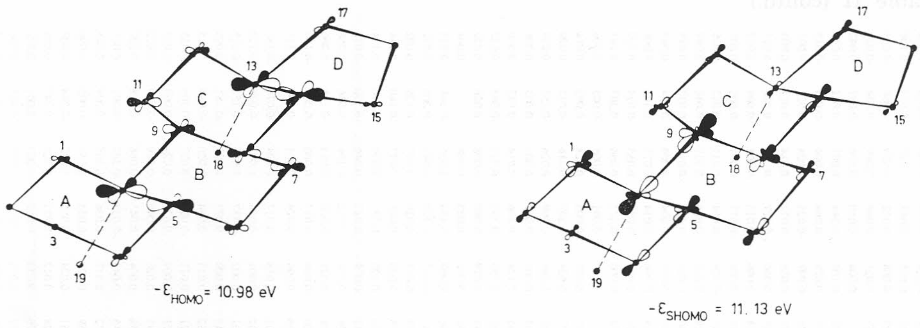

Figure 1. The transversal (T-type) and longitudinal (L-type) ribbon-like MO's of 5α-androstane, according to MNDO results.

nounced shift of σ-systems towards higher energies, whereas in the low energy region a new system appears. It corresponds to the carbonyl oxygen lone pair ionization. Nevertheless it is not strictly localized on the oxygen atom but is rather mixed with the steroid ribbon-type orbital giving rise to significant delocalization. This is supported not only by MNDO calculations (see Table II) but is also evident from the vibrational structure broadening in the related PE band.

The details of the perturbation caused by this highly electronegative group can be closely studied in the PE spectra of a series of monoketones over diketones to triketones. According to the calculated electron density distribution, the carbonyl group would mix either with T- or L-type orbital depending on the position of substitution. Namely, in 3-one case HOMO is of T-type, in 17-one case it is of L-type, while in 11-one case HOMO could be described as a mixture of both types of orbitals (T- plus L-type). In 3,17-dione HOMO and SHOMO are closely related to HOMO's of the corresponding monoketones, *i. e.*, it seems that no interaction has taken place. It should be pointed out that no geometry optimization has been performed for *4*, since it is known that through-bond interaction is sensitive not only to the number and parity of bonds between two centers, but also on the assumed molecular geometry.

The interpretation of the PE spectrum of 3,11,17-trione could be supported by the results available from monoketones and 3,17-diketone. The low energy part of the spectrum of *6* reveals three electron systems. *Per analogiam* with PE spectra of *2* and *5* one deduces that the middle system appearing at 9.09 eV could be assigned to the almost unperturbed carbonyl oxygen lone pair in A ring. On the contrary, the other two systems at 8.90 and 9.50 eV, respectively, should correspond to ionizations from significantly mixed wave functions of 11-and 17-carbonyl groups. That is nicely reproduced in diagramatic representation of MNDO electron density distribution (Figure 2). Even the experimentally observed splitting amounting to 0.60 eV is correctly predicted by this calculation ($\Delta\varepsilon^{\mathrm{MNDO}}(n_{\mathrm{O}}) = 0.59$ eV). Taking into account relative orien-

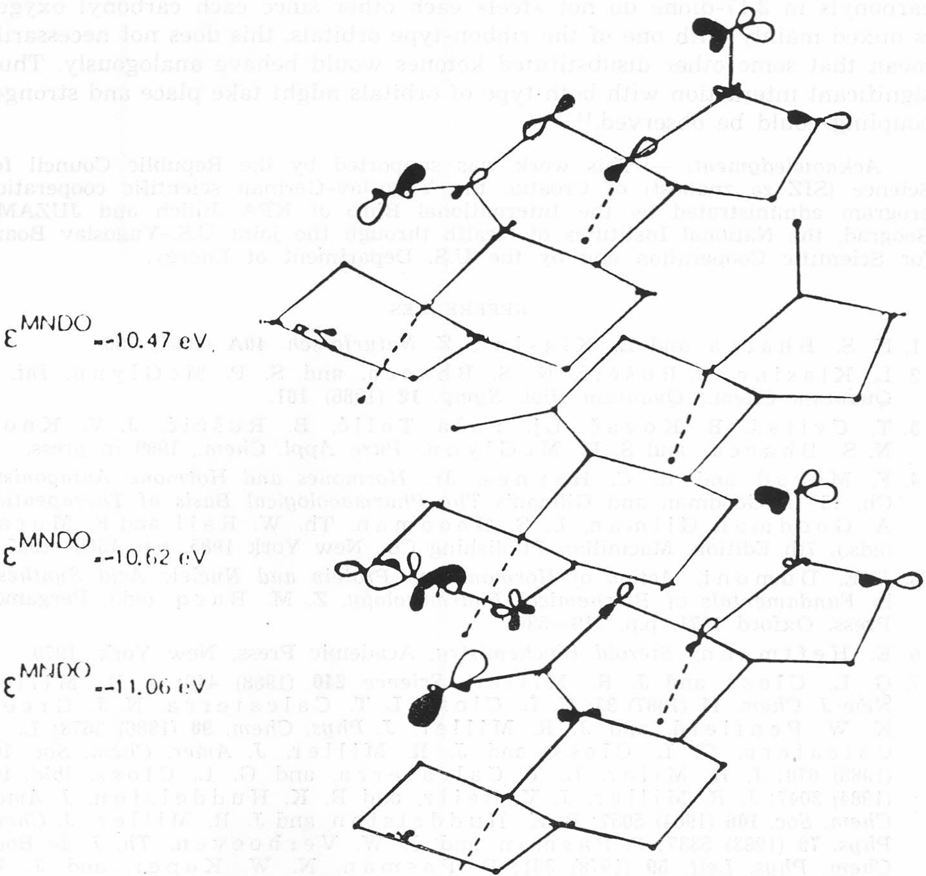

Figure 2. The three highest occupied MO's of 5α-androstane-3,11,17-trione on the basis of MNDO calculations.

tation of two oxygen atoms and their interatomic distance which, according to the MNDO calculations amounts to 540 pm, this prominent coupling could be due to through bond interaction. On the other hand, no interaction is observed between the carbonyl group in ring A and either of the carbonyl groups in C or D rings. This is confirmed by MNDO calculations, since no participation from oxygen lone pair electrons in 11- and 17-positions is found in the SHOMO of *6* (which corresponds to the oxygen lone pair on 3-position; see Figure 2). Such a theoretical result is not surprising as these two oxygen atoms are 8 and 10 σ_{CC} bonds apart from the one in 3-position, respectively.

The close study of long-range interactions gives insight into the type and extent of orbital mixing. As we have seen the position of a carbonyl group is by no means irrelevant (*e. g.*, positions 3- *vs.* 17- *vs.* 11-). In each case the type of orbital mixing is different and therefore the effect of coupling between two or three carbonyl groups differs significantly. Although two carbonyls in 3,17-dione do not »feel« each other since each carbonyl oxygen is mixed mainly with one of the ribbon-type orbitals, this does not necessarily mean that some other disubstituted ketones would behave analogously. Thus, significant interaction with both type of orbitals might take place and stronger coupling could be observed.[14]

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SAŽETAK

Fotoelektronski spektri, MNDO izračunavanja i elektronska struktura nekih zasićenih steroida

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Fotoelektronski spektri, semiempirijska MNDO SCF MO izračunavanja (uz pretpostavku valjanosti Koopmanova teorema) te empirijske činjenice korištene su za određivanje strukture (valentnih) elektrona 5α-androstana (*1*), 5α-androstan-3-ona (**2**), 5α-androstan-11-ona (**3**), 5α-androstan-17-ona (**4**), 5α-androstan-3,17-diona (*5*) i 5α-androstan-3,11,17-triona (*6*).