

**Photoelectron (HeI) Spectroscopy of Flavonoids
and Thioflavonoids, I.
Molecular Orbitals and Ionization Potentials
of Chalcone, Aurone, and 1-Thioaurone**

Zoltán Dinya, István Komáromi, and Ferenc Sztaricskai*

*Research Group for Antibiotics of the Hungarian Academy of Sciences,
H-4010 Debrecen, Hungary*

Albert Lévai and György Litkei

Department of Organic Chemistry, Kossuth University, H-4010 Debrecen, Hungary

Received March 2, 1992

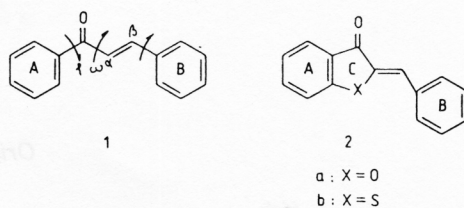
Electronic structure of chalcone (**1**), aurone (**2a**) and 1-thioaurone (**2b**) has been studied by measuring their HeI PE spectra and the interpretation of data has been performed by means of semiempirical molecular orbital calculations (PMO, HAM/3, and CNDO/S).

INTRODUCTION

Flavonoids are well-known natural products and some of them are used as medicines as well.¹ For the sake of a better understanding of their chemical properties and structure-activity relationships, a knowledge of their electronic structure is especially important. Several research groups have already studied the electronic structure of various flavonoids.² Molecular orbitals and ionization potentials of such compounds were studied mainly by theoretical means. First experimental results, the vertical ionization potential values of chalcone (**1**) derivatives, were published by us in 1975.³

No ultraviolet photoelectron spectral (UPS HeI) data of flavonoids have hitherto been published. However, the UPS properties of some structural units of flavonoids, *e.g.* γ -pyrone,^{4,5} its thio analogue^{4,5} and the oxidized thio derivatives,⁶ chromone and 1-thiochromone⁷ are known. As a continuation of our previous studies,^{2a,i,j,3} experimental and theoretical investigations of the electronic structure of chalcone (**1**), aurone (**2a**) and 1-thioaurone (**2b**) by means of photoelectron (PE) spectroscopy (HeI) and MO calculations are reported in our present paper.

* Author to whom correspondence should be addressed.



Scheme 1.

Quantum chemical calculations can advantageously be utilized for the assignment of the photoelectron spectra since these methods help to predict the nature and ordering of the molecular orbitals. Correlation of the calculated and experimental data is performed by using Koopmans' theorem⁸, implying the »frozen orbital« approximation in the ion and in the neutral molecule. When the errors due to these two approximations do not cancel out, Koopmans' theorem fails and the calculated eigenvalues have to be corrected before applying them to UPS. According to the results of Buemi and Zuccarello,⁹ a class of compounds for which the breakdown of Koopmans' theorem seems to be a common feature are the α,β -unsaturated carbonyl compounds. For chalcone (**1**), accurate calculations of molecular ionization energies (I 's) are time consuming and, according to the results of Buemi and Zuccarello,⁹ relaxation and correlation effects should also be taken into consideration. The aim of the present paper is a reinvestigation of this molecule by adopting the HAM/3 method¹⁰⁻¹² which, in its UPS option, minimizes errors due to electron relaxation and correlation energies, giving eigenvalues in very good agreement⁹ with the experimental ones in the whole HeI PE spectrum.

EXPERIMENTAL AND CALCULATIONS

The compounds studied (**1**, **2a** and **2b**) were prepared as described in the literature and their purity was checked by NMR and mass spectroscopy. The gas phase HeI PE spectra were obtained with a Perkin-Elmer PS 18 photoelectron spectrometer and were internally calibrated against Xe and Ar lines. Band locations are characterized by the positions of the band maxima considered to correspond to the vertical ionization energies (I 's). Reproducibility was better than ± 0.05 eV and the accuracy of the I values was estimated to be ± 0.05 eV where two decimal places are quoted, otherwise ± 0.1 eV. HAM/3 and CNDO/S¹³ quantum chemical calculations were performed by the AM1 method¹⁴ for optimized geometries. In the case of 1-thioaurone (**2b**), only CNDO/S calculation was performed since, owing to the lack of parameters, the HAM/3 method cannot be used for sulfur-containing compounds. Data are in accordance with our former results¹⁵ and with the published experimental¹⁶⁻²⁰ and theoretical²¹ ones and unequivocally prove that for the *trans*-chalcone ($1:\phi:12.5^\circ$, $\theta:31.5^\circ$ and $\psi:14^\circ$) the quasiplanar *s-cis* conformation is favoured. In the case of aurone (**2a**) and 1-thioaurone (**2b**), the dihedral angle between the heterocyclic ring and the phenyl moiety was 20° , determined by AM1 optimization. Calculations have been performed for the planar *s-trans* conformation of the *trans*-chalcone as well and it has been found that the photoelectron spectrum is independent of the chalcone conformation. For this reason, only theoretical data optimized by the AM1 method are presented.

RESULTS AND DISCUSSION

HeI PE spectrum of chalcone (**1**) is shown in Figure 1 and the IE values, together with the assignment, are listed in Table I. Three broad bands are observed in the PE

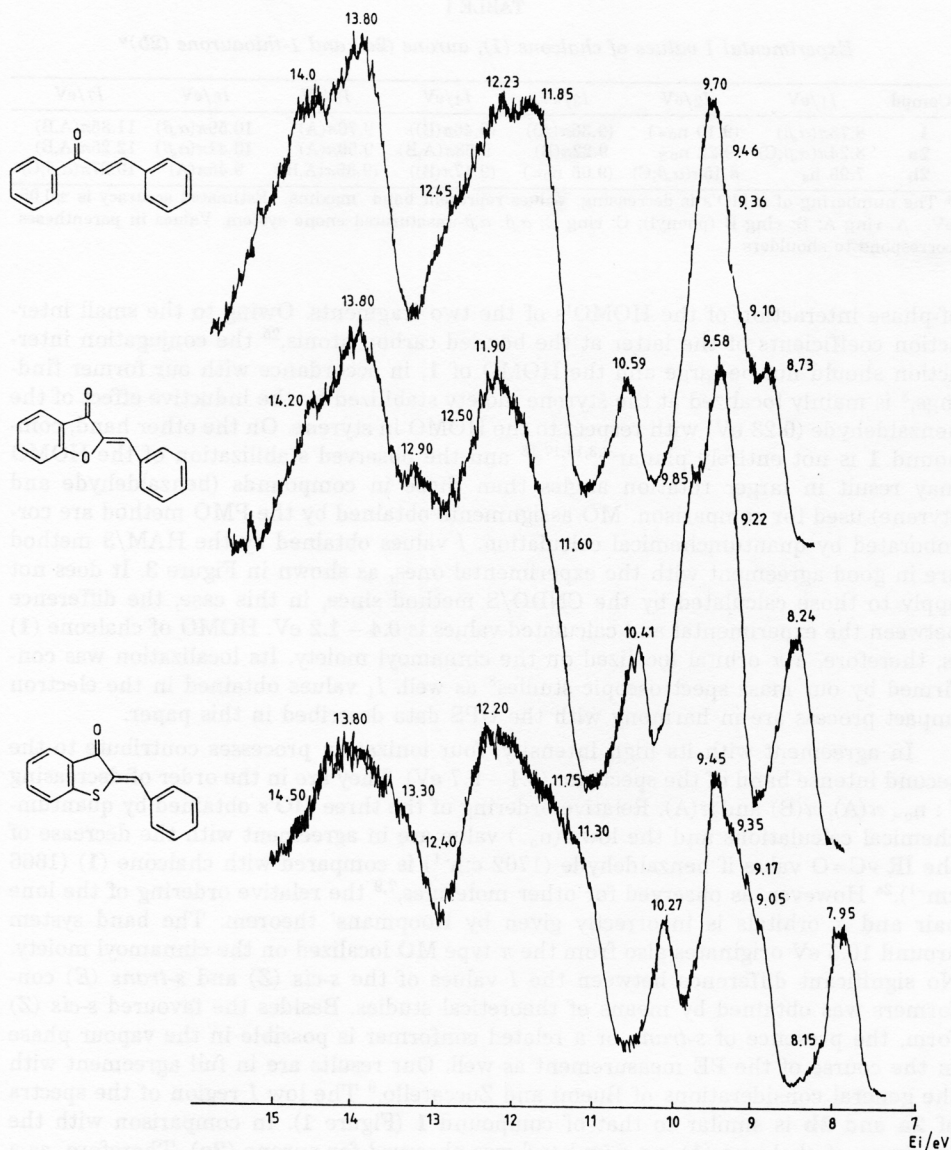


Figure 1. Low-energy regions of the HeI PE spectra of (a) chalcone (**1**), (b) aurone (**2a**) and (c) 1-thioaurone (**2b**)

spectrum (Figure 1) of chalcone (**1**) between 8 and 12 eV. On the basis of the PMO theory,²² chalcone (**1**) can be considered to be derived from the interaction of benzaldehyde and styrene^{23,24} (Figure 2). The HOMO of compound **1** originates from the out-

TABLE I

*Experimental I values of chalcone (1), aurone (2a) and 1-thioaurone (2b)**

Compd.	I_1/eV	I_2/eV	I_3/eV	I_4/eV	I_5/eV	I_6/eV	I_7/eV
1	$8.73\pi(\alpha,\beta)$	(9.10 $n_{0=}$)	(9.36 π (A))	(9.46 π (B))	9.70 π (A)	10.59 $\pi(\alpha,\beta)$	11.85 π (A,B)
2a	8.24 $\pi(\alpha,\beta;\text{C})$	9.22 $n_{0=}$	9.22 π (B)	9.58 π (A,B)	9.50 π (A)	10.41 $\pi(\alpha,\beta)$	12.25 π (A,B)
2b	7.95 n_s	8.15 $\pi(\alpha,\beta;\text{C})$	(9.05 $n_{0=}$)	(9.17 π (B))	(9.35 π (A,B))	9.45 π (A)	10.27 $\pi(\alpha,\beta;\text{C})$

* The numbering of π MO's is decreasing. Values represent band maxima. Estimated accuracy is ± 0.05 eV. A: ring A; B: ring B (phenyl); C: ring C; α,β : α,β -unsaturated enone system. Values in parentheses correspond to shoulders

of-phase interaction of the HOMO's of the two fragments. Owing to the small interaction coefficients of the latter at the bonded carbon atoms,²⁵ the conjugation interaction should not be large and the HOMO of **1**, in accordance with our former findings,³ is mainly localized at the styrene moiety stabilized by the inductive effect of the benzaldehyde (0.23 eV) with respect to the HOMO in styrene. On the other hand, compound **1** is not entirely planar^{21,3,15,17,18} and the observed stabilization of the HOMO may result in larger rotation angles than those in compounds (benzaldehyde and styrene) used for comparison. MO assignments obtained by the PMO method are corroborated by quantumchemical calculation. I values obtained by the HAM/3 method are in good agreement with the experimental ones, as shown in Figure 3. It does not apply to those calculated by the CNDO/S method since, in this case, the difference between the experimental and calculated values is 0.4 – 1.2 eV. HOMO of chalcone (**1**) is, therefore, a π orbital localized on the cinnamoyl moiety. Its localization was confirmed by our mass spectroscopic studies³ as well. I_1 values obtained in the electron impact process are in harmony with the UPS data described in this paper.

In agreement with its high intensity, four ionization processes contribute to the second intense band of the spectrum (9.1 – 9.7 eV). They are in the order of decreasing I : $n_{0=}$ π (A), π (B) and π (A). Relative ordering of the three MO's obtained by quantumchemical calculations and the low $I(n_{0=})$ value are in agreement with the decrease of the IR $\nu\text{C}=\text{O}$ value if benzaldehyde (1702 cm^{-1}) is compared with chalcone (**1**) (1666 cm^{-1}).^{2a} However, as observed for other molecules,^{7,9} the relative ordering of the lone pair and π orbitals is incorrectly given by Koopmans' theorem. The band system around 10.5 eV originates also from the π type MO localized on the cinnamoyl moiety. No significant difference between the I values of the *s-cis* (*Z*) and *s-trans* (*E*) conformers was obtained by means of theoretical studies. Besides the favoured *s-cis* (*Z*) form, the presence of *s-trans* or a related conformer is possible in the vapour phase in the course of the PE measurement as well. Our results are in full agreement with the general considerations of Buemi and Zuccarello.⁹ The low I region of the spectra of **2a** and **2b** is similar to that of compound **1** (Figure 1). In comparison with the spectrum of chalcone (**1**), no new band was observed for aurone (**2a**). Therefore, as a result of the inductive effect of the ethereal oxygen and the ring strain, its MO's can be considered as shifted chalcone orbitals (Figure 4). Figure 4 shows that the I values obtained by the HAM/3 method are in good agreement with the experimental data. The HOMO level is unambiguously the π orbital localized onto the styryl moiety and extended to the carbonyl group and ethereal oxygen. On the basis of the HAM/3 calculation, the level of the lone-pair electron of ethereal oxygen should be at approx. 11.3 eV and some π type MO's are given between 11.5 and 12 eV values. In the spectrum, a broad band system is found at about 12.5 eV. A possible reason is that the HAM/3

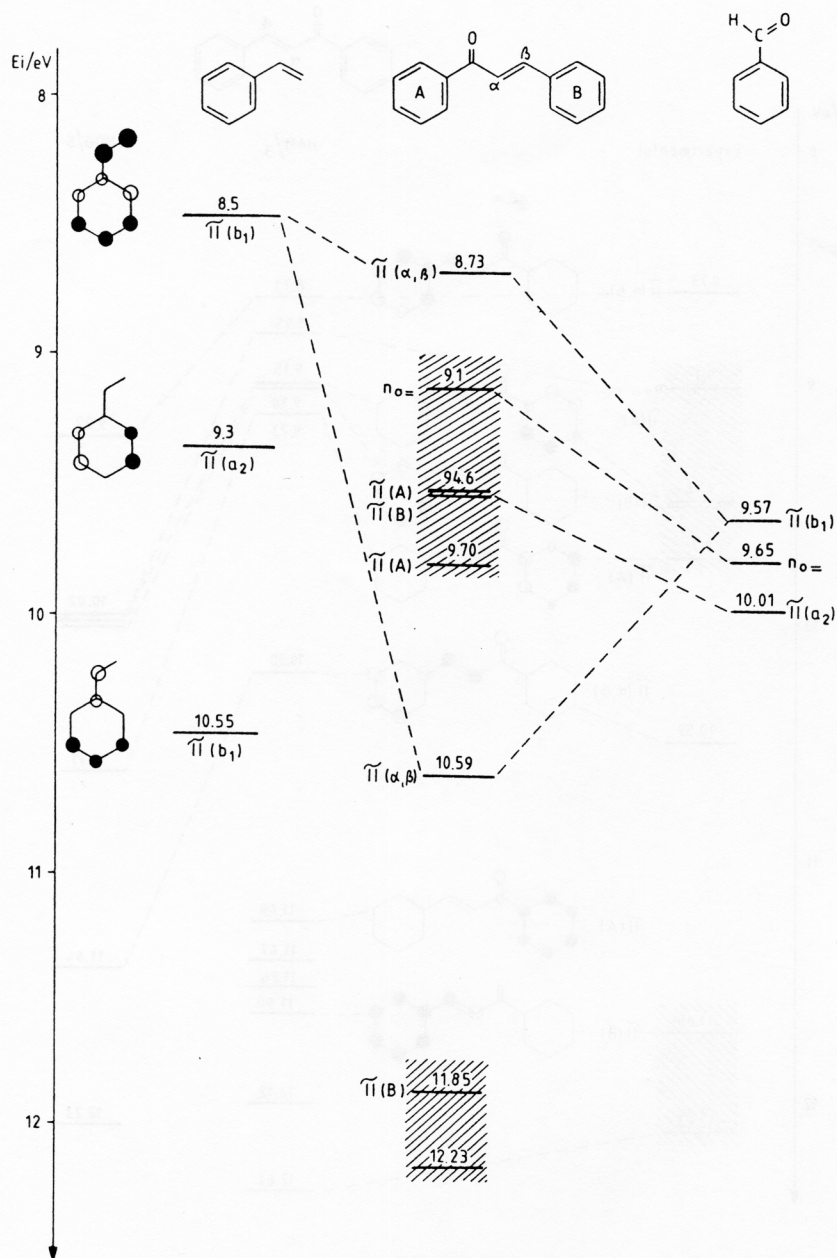


Figure 2. PMO interaction diagram of chalcone (1) (○ positive, ● negative)

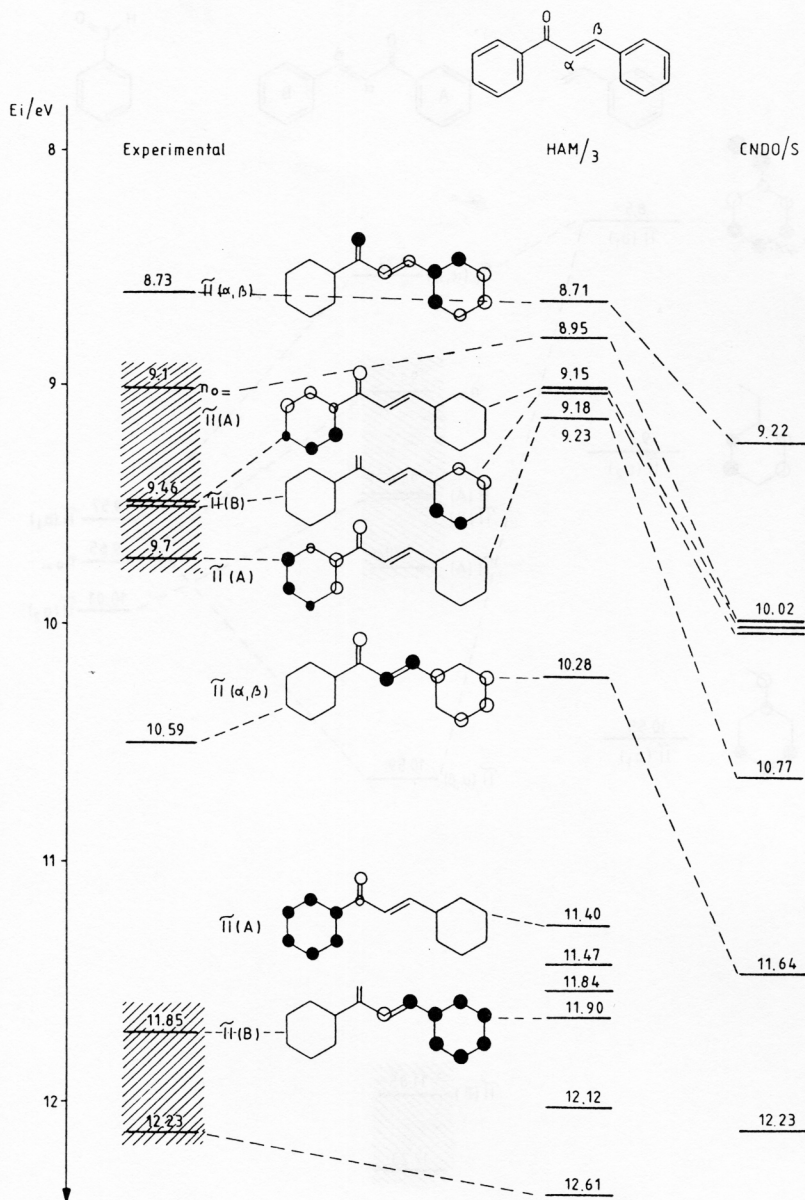


Figure 3. Experimental and theoretical UPS data of chalcone (1) (○ positive, ● negative)

method is less reliable for the strained heterocyclic systems in the higher I region (above 11 eV). The HOMO of aurone (2a) is less stable by 0.2 eV if compared with

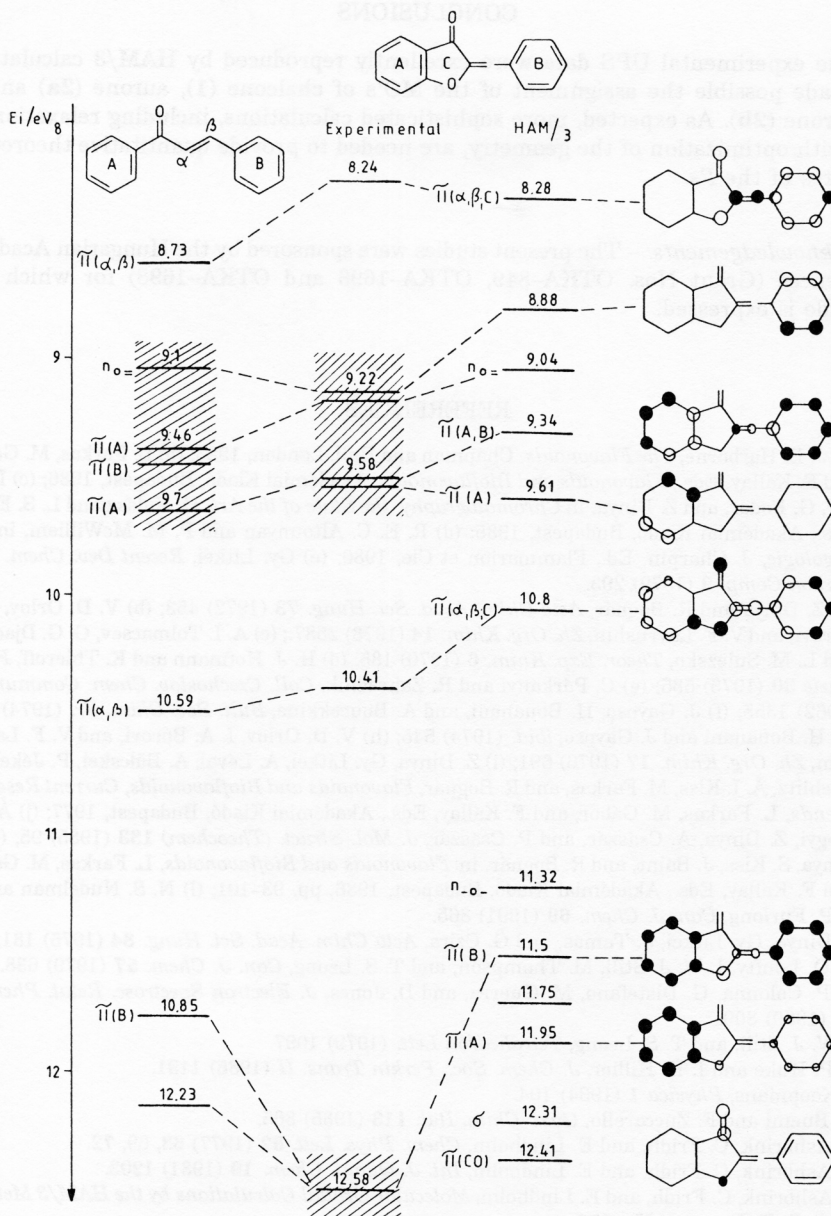


Figure 4. Experimental and theoretical (HAM/3) UPS data of aurone (**2a**) (○ positive, ● negative)

the flavone while its n_o orbital is more stable by 0.4 eV in the same comparison. HeI PE properties of 1-thioaurone (**2b**) are analogous to those of the aurone (**2a**).

CONCLUSIONS

The experimental UPS data were excellently reproduced by HAM/3 calculations and made possible the assignment of the MO's of chalcone (**1**), aurone (**2a**) and 1-thioaurone (**2b**). As expected, more sophisticated calculations, including relaxation effects with optimization of the geometry, are needed to provide quantitative theoretical estimates of the I 's.

Acknowledgements. – The present studies were sponsored by the Hungarian Academy of Sciences (Grant Nos. OTKA-849, OTKA-1696 and OTKA-1698) for which our gratitude is expressed.

REFERENCES

1. (a) J. B. Harborne, *The Flavonoids*, Chapman and Hall, London, 1988; (b) L. Farkas, M. Gábor, and F. Kállay, Eds., *Flavonoids and Bioflavonoids*, Akadémiai Kiadó, Budapest, 1986; (c) I. Fodor, G. Fodor, and Z. Dinya, in *Chromatography, the State of the Art*, H. Kalász and L. S. Ettre, Eds., Akadémiai Kiadó, Budapest, 1985; (d) R. E. C. Altounyan and P. M. McWilliam, in: *Allergologie*, J. Charpin, Ed., Flammarion et Cie, 1980; (e) Gy. Litkei, *Recent Dev. Chem. Nat. Carbon Comp.* **9** (1979) 293.
2. (a) Z. Dinya and R. Bognár, *Acta Chim. Acad. Sci. Hung.* **73** (1972) 453; (b) V. D. Orlov, I. A. Borovi, and V. F. Lavrushin, *Zh. Org. Khim.* **14** (1978) 2587.; (c) A. I. Tolmacsev, G. G. Djadusa, and L. M. Sulezsko, *Theor. Exp. Khim.* **6** (1970) 185; (d) H. J. Hofmann and K. Thieroff, *Pharmazie* **30** (1975) 585; (e) C. Párkányi and R. Zahradnik, *Coll. Czechoslov. Chem. Commun.* **27** (1962) 1355; (f) J. Gayoso, H. Bouanani, and A. Boucekkine, *Bull. Soc. Chim. Fr.* (1974) 538; (g) H. Bouanani and J. Gayoso, *ibid.* (1974) 545; (h) V. D. Orlov, I. A. Borovi, and V. F. Lavrushin, *Zh. Org. Khim.* **17** (1976) 691; (i) Z. Dinya, Gy. Litkei, A. Lévai, A. Bölcskei, P. Jékel, Sz. Rochlitz, Á. I. Kiss, M. Farkas, and R. Bognár, *Flavonoids and Bioflavonoids, Current Research Trends*, L. Farkas, M. Gábor, and F. Kállay, Eds., Akadémiai Kiadó, Budapest, 1977; (j) Á. Somogyi, Z. Dinya, A. Császár, and P. Császár, *J. Mol. Struct. (Theochem)* **133** (1985) 95; (k) Z. Dinya, S. Kiss, J. Báint, and R. Bognár, in: *Flavonoids and Bioflavonoids*, L. Farkas, M. Gábor, and F. Kállay, Eds., Akadémiai Kiadó, Budapest, 1986, pp. 93–101; (l) N. S. Nudelman and J. J. P. Furlong, *Can. J. Chem.* **69** (1991) 865.
3. Z. Dinya, Gy. Litkei, J. Tamás, and G. Czira, *Acta Chim. Acad. Sci. Hung.* **84** (1975) 181.
4. R. O. Loufty, I. W. J. Still, M. Thompson, and T. S. Leong, *Can. J. Chem.* **57** (1979) 638.
5. F. P. Colonna, G. Distefano, M. Guerra, and D. Jones, *J. Electron Spectrosc. Relat. Phenom.* **18** (1980) 309.
6. I. W. J. Still, and T. S. Leong, *Tetrahedron Lett.* (1979) 1097.
7. J. P. Huke and I. H. Hillier, *J. Chem. Soc., Perkin Trans. II* (1985) 1191.
8. T. Koopmans, *Physica* **1** (1934) 104.
9. G. Buemi and F. Zuccarello, *Gazz. Chim. Ital.* **113** (1985) 865.
10. L. Ashbrink, C. Fridh, and E. Lindholm, *Chem. Phys. Lett.* **52** (1977) 63, 69, 72.
11. L. Ashbrink, C. Fridh, and E. Lindholm, *Int. J. Quant. Chem.* **19** (1981) 1203.
12. L. Ashbrink, C. Fridh, and E. Lindholm, *Molecular Orbital Calculations by the HAM/3 Method*, Q. C. P. E. Program No. 393.
13. L. Ashbrink, C. Fridh, and E. Lindholm, *ibid.* Q. C. P. E. Program No. 333.
14. L. Ashbrink, C. Fridh, and E. Lindholm, *Dewar's General Molecular Orbital Package*, Q. C. P. E. Program No. 455.
15. Z. Dinya, Á. I. Kiss, and G. Pongor, *Acta Chim. Acad. Sci. Hung.* **98** (1978) 77.
16. G. Montauda, V. Librando, S. Caccamese, and P. Maravigna, *J. Amer. Chem. Soc.* **95** (1975) 6365.
17. D. Rabinovich, *J. Chem. Soc. Sect. B* (1970) 11.

18. D. Rabinovich, and Z. Shakhed, *Acta Cryst. Sect. B* **30** (1974) 2829.
19. Z. Dinya and Gy. Litkei, *Acta Chim. Acad. Sci. Hung.* **77** (1973) 211.
20. K. Bowden, C. K. Duah, and R. J. Ranson, *J. Chem. Soc., Perkin Trans. II* (1991) 109.
21. N. S. Nudelman and J. J. P. Furlong, *Can. J. Chem.* **69** (1991) 865.
22. M. J. S. Dewar and R. C. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975.
23. C. N. R. Rao, P. K. Basu, and M. S. Hidge, *Appl. Spectr. Rev.* **15** (1979) 1.
24. L. J. P. Tolić, B. Kovač, L. Klasinc, S. M. Shevchenko, and S. P. McGlynn, *Int. J. Quantum Chem. Symp. QBS* **24** (1990) 799.
25. J. W. Relsders and R. I. Coltran, *J. Electron Spectr. Relat. Phenom.* **18** (1980) 309.

SAŽETAK

**He(I) fotoelektronski spektri flavonoida i tioflavonoida I.
Molekulske orbitale i energije ionizacije kalcona, aurona i 1-tioaurona**

*Zoltán Dinya, István Komáromi, Ferenc Sztaricskai,
Albert Lévai i György Litkei*

Na temelju sprege He(I) fotoelektronspektroskopskih mjerenja i rezultata semiempirijskih kvatno-kemijskih računa razmotrena je elektronska struktura kalcona, aurona i 1-tioaurona.