Photoelectron (HeI) Spectroscopy of Flavonoids and Thioflavonoids, II. Photoelectron Spectra of Chromone and 1-Thiochromone Derivatives

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HeI photoelectron spectra of some chromanone and chromone derivatives (flavanone, isoflavanone, flavone and isoflavone), their thio analogues, and sulfoxide and sulfone derivatives, respectively, have been measured in the gas phase and the data evaluated by means of semiempirical molecular orbital evaluations (HAM/3 and CNDO/S) and by the PMO theory.

INTRODUCTION

As a continuation of our previous paper and former studies on γ-pyrone derivatives, photoelectron spectroscopic and theoretical investigations of chromanones and chromones, their thio analogues and the oxidized derivatives of the latter (Scheme 1) are reported in our present paper.

UPS properties and their evaluation of γ-pyrone and thio analogue have been published by Distefano et al. UPS data, together with a qualitative interpretation of 1-thiochromanone (2d), 1-thiochromone (3i) and their sulfoxides and sulfones, respectively, were described by Still et al. in 1979. HeI PES of chromone (3a) and 1-thiochromone (3i) were measured and discussed by Huke and Hillier by means of ab initio calculations and on the basis of the common PMO theory. Four highest oc-

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cupied MO's of chromone (3a) (9.13, 9.13, 9.67 and 10.20 eV) are evaluated by these authors on the basis of the PMO theory and starting from the experimental UPS data of phenol and acrolein and are considered to be of \( \pi_1 \), \( n_{o-r} \), \( \pi_2 \) and \( \pi_3 \) character. This assignment was considered to be valid for the 1-thiochromone (3i), as well. It was emphasized that the replacement of the sulfur by oxygen in compound 3a resulted in unchanged \( \pi_2 \) and \( \pi_3 \) values but in an enhanced \( \pi_1 \) energy with a considerable oxygen component. In the case of the 1-thiochromone (3i), the first band of chromone (3a) is split into two components and the low-energy peak is due to the \( \pi_1 \). \textit{Ab initio} STO-3G values were found to differ from the experimental data generally by more than 2 eV.

Since no UPS data of chromone derivatives, \textit{e.g.} chromone (3a), flavone (3b), iso-flavone (3c) and their thio analogues (3d - 3k) have hitherto been published, the primary aim of our present work was to study such properties of these substances. It should also be mentioned that only few PES of sulfoxides and sulfones have hitherto been published\(^{10-16} \) and, therefore, our present studies are a novel contribution to the known data.

### EXPERIMENTAL AND CALCULATIONS

The compounds investigated were prepared according to known methods.\(^{6,7,17,18} \) Purity of the samples was checked by various spectroscopic techniques. Conditions of the measurement of the HeI photoelectron spectra and the accuracy of the measurements were discussed in our previous paper.\(^1 \) For the sulfur-free compounds, quantumchemical calculations were performed by HAM/3\(^{19-21} \) CNDO/S\(^{22} \) and AM1\(^{23} \) semiempirical methods. Because of the lack of appropriate parameters, HAM/3 method cannot be used for the sulfur-containing compounds. Starting from standard geometric and X-ray data,\(^{24-26} \) complete geometry optimization has been performed for our compounds (2a - 2f and 3a - 3b) by means of the AM1 method. HAM/3 and CNDO/S calculations were then performed for the optimized geometries. Influence of the optimization of geometry was investigated for chromone (3a) by the HAM/3 method and it was concluded that the optimized geometries provide good agreement between the experimental and theoretical HeI PES values. Heterocyclic ring of the chromanone derivatives (Scheme 1), \textit{e.g.} flavanone (2b),
TABLE I

Experimental I values of chromanone and chromone derivatives and their thio analogues\textsuperscript{a-c}

<table>
<thead>
<tr>
<th>Compound</th>
<th>$I_1$/eV</th>
<th>$I_2$/eV</th>
<th>$I_3$/eV</th>
<th>$I_4/3V$</th>
<th>$I_5$/eV</th>
<th>$I_6$/eV</th>
<th>$I_7$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>8.74π(A)</td>
<td>9.44π(A)</td>
<td>9.44n₀=</td>
<td>11.28π(C) + n₉₀=</td>
<td>11.84</td>
<td>12.20</td>
<td>12.60</td>
</tr>
<tr>
<td>2b</td>
<td>8.75π(A)</td>
<td>(9.10π(Ph))</td>
<td>9.52π(A)</td>
<td>9.52n₀=</td>
<td>9.52π(Ph)</td>
<td>(11.20π(Ph))</td>
<td>(11.70n₉₀=)</td>
</tr>
<tr>
<td>2c</td>
<td>8.75π(A)</td>
<td>(9.15π(Ph))</td>
<td>9.46π(A)</td>
<td>9.46n₀=</td>
<td>9.46π(Ph)</td>
<td>(11.15π(A))</td>
<td>11.70n₉₀=</td>
</tr>
<tr>
<td>2d</td>
<td>8.37π(A) + nₙ₀</td>
<td>9.47π(C)</td>
<td>9.47n₀=</td>
<td>10.27π(C)</td>
<td>11.30</td>
<td>12.00</td>
<td>12.50</td>
</tr>
<tr>
<td>2e</td>
<td>8.24π(A) + nₙ₀</td>
<td>(9.10π(Ph))</td>
<td>9.45π(A)</td>
<td>9.45n₀=</td>
<td>9.45π(Ph)</td>
<td>10.30π(A)</td>
<td>11.10</td>
</tr>
<tr>
<td>2f</td>
<td>7.94nₙ₀ + π(SO)</td>
<td>9.41n₀=</td>
<td>9.41n₀=</td>
<td>10.27π(Ph)</td>
<td>11.30π(SO)</td>
<td>11.80</td>
<td></td>
</tr>
<tr>
<td>2g</td>
<td>(9.40n₀=)</td>
<td>9.77π(A)</td>
<td>9.77π(Ph)</td>
<td>10.51π(A)</td>
<td>11.10π(SO₂)</td>
<td>11.68π(SO₂) + π(SO₂)</td>
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</tr>
<tr>
<td>3a</td>
<td>8.95π(C)</td>
<td>9.08n₀=</td>
<td>9.62π(A)</td>
<td>10.18π(C)</td>
<td>12.10n₉₀=</td>
<td>12.20π</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>8.66π(C)</td>
<td>9.04n₀=</td>
<td>9.04π(Ph)</td>
<td>9.60π(A,Ph)</td>
<td>9.60π(Ph)</td>
<td>10.42π(C,Ph)</td>
<td>11.80n₉₀=</td>
</tr>
<tr>
<td>3c</td>
<td>8.55π(C)</td>
<td>9.00n₀=</td>
<td>9.24π(Ph)</td>
<td>9.24π(A)</td>
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<td>11.50n₉₀=</td>
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<tr>
<td>3d</td>
<td>8.29π(C)</td>
<td>9.10n₀=</td>
<td>9.30π(Ph)</td>
<td>9.52π(A)</td>
<td>9.52π(Ph)</td>
<td>10.13π(C)</td>
<td>11.40π(S)</td>
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<tr>
<td>3e</td>
<td>7.75nₙ₀</td>
<td>7.88π(C)</td>
<td>9.14π(Ph)</td>
<td>(9.30π(A))</td>
<td>9.54π(Ph)</td>
<td>10.28π(C)</td>
<td>11.46π(S)</td>
</tr>
<tr>
<td>3f</td>
<td>7.73nₙ₀</td>
<td>7.73π(C) + nₙ₀=</td>
<td>9.00π(Ph)</td>
<td>(9.10π(A))</td>
<td>9.47π(Ph)</td>
<td>10.14π(C)</td>
<td>10.38π(S)</td>
</tr>
<tr>
<td>3g</td>
<td>8.90π + nₙ₀(c)</td>
<td>9.57n₀=</td>
<td>9.57π(A)</td>
<td>9.57π(Ph)</td>
<td>10.30π(SO)</td>
<td>10.76π(C)</td>
<td>11.33π(SO)</td>
</tr>
<tr>
<td>3h</td>
<td>(9.40nₙ₀= + n₀=)</td>
<td>9.72π(A)</td>
<td>9.72π(Ph)</td>
<td>9.72π(Ph)</td>
<td>10.37π(C)</td>
<td>10.70π(SO₂)</td>
<td>11.80π(SO₂) + π(SO₂)</td>
</tr>
<tr>
<td>3i</td>
<td>8.52π(C)</td>
<td>9.18n₀=</td>
<td>9.59π(A)</td>
<td>10.08π(C)</td>
<td>11.60π(S)</td>
<td>11.79π</td>
<td>12.30π</td>
</tr>
<tr>
<td>3j</td>
<td>7.98nₙ₀</td>
<td>8.25π(C)</td>
<td>9.40π(A)</td>
<td>9.94π(C)</td>
<td>9.84π(C)</td>
<td>11.30</td>
<td>11.63π</td>
</tr>
<tr>
<td>3k</td>
<td>7.92nₙ₀</td>
<td>8.04π(C)</td>
<td>9.18π(A)</td>
<td>11.40π</td>
<td>11.60π(S)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Phenyl ring at C-2 or C-3 is regarded as π(Ph)  
\textsuperscript{b} Α = mainly localized on ring A; C = mainly localized on ring C  
\textsuperscript{c} Values in parentheses correspond to shoulders
isoflavonone (2c) and their thio analogues, adopts a half-chair conformation and the phenyl moiety at position 2 or 3 is equatorial.

Our results are in accord with the literature data. Chromone (3a) is planar and, therefore, in this case optimization of the dihedral angle between the chromone skeleton and phenyl group at position 2 or 3 was important. Dihedral angle was 30 – 32° for the flavone derivatives and 42 – 44° for the isoflavones, which is in good agreement with the published data. Further details of the quantumchemical calculations will be published in a separate paper.

RESULTS AND DISCUSSION

Experimental I values and their assignments of the compounds studied (2a – 2f and 3a – 3k) are summarized in Table I. Figure 1 shows the HeI PES of chromone (3a) and some thio analogues (3a – 3k). MO’s involved in ionization processes producing the first few bands of the PE spectra can be derived from the spectra of butadiene, γ-pyrole and its thio analogues as shown in Figure 2 for chromone (3a). This seems to be a better approximation than that supposed by Huke and Hillier. Interactions between all MO’s with C₈ symmetry are allowed. However, taking into consideration the energy difference between the first two MO’s of the γ-pyrole and the

![Figure 1. Low-energy of the HeI PE spectra of chromone (3a), 1-thiocromone (3i), 4-thiocromone (3j), 1,4-dithiocromone (3f), chromanone (2a) and 1-thiochromanone (2d).]
Figure 2. PMO interaction diagram of chromone (3a) (○ positive, ● negative).
Figure 3. Experimental and theoretical UPS data of chromone (3a (O positive, • negative).
butadiene in the first approach, there is a weak interaction between the HOMO’s of the two fragments but not with the inner π MO, while the π(1) of the butadiene interacts with the π(a) of the γ-pyrene. As a result of the decreasing inductive effect, destabilization is observed in direction from 3a to 3k. HAM/3 data and CNDO/S theoretical data of chromone (3a) and the assignment of the appropriate energy levels are shown in (Figure 2). It can be concluded that the results obtained by the HAM/3 method are in good agreement with the experimental data but this is not true of those calculated with CNDO/S. On the basis of the findings of Huke and Hillier and our present studies, the HAM/3 method provides better results than the ab initio method on STO–3G or 3–21G basis. HAM/3 data (Figure 2) unequivocally prove that the HOMO of chromone (3a) is mainly a π orbital localized on ring C. It can be stated that the nπ* energy level of chromone (3a), owing to the quasiaromatic character of the heterocyclic ring, is more stable than in the case of γ-pyrene (1a). Data in Table I prove that the HOMO of the carbonyl compounds 3a and 3i is a π MO while that of the thiocarbonyl derivatives 3j and 3k is an nπ* type MO. Relative order of the orbitals, except for substance 3a where this is opposite, is the same as found for γ-pyrones (1a – 1d). According to our HAM/3 calculations, in the case of compound 3a, this inversion (Figure 3) is a consequence of a more intense interaction between the two fragments. On the basis of our calculations, in the case of the 1-thio compounds, the nπ* ionization should appear at approx. 9.5 eV but, owing to the known error of the CNDO/S method, this may differ by about ±0.5 eV. In the spectrum of compound 3k, the band appearing at 10.65 eV cannot be considered as a π MO. Our AM1 and CNDO/S calculations reveal that this should originate from the ionization of a σ MO localized mainly on the sulfur atom. In the spectrum (Figure 1), it is overlapped by the band at 11.40 eV belonging to a π MO. PE spectra of 2a and 2d (Figure 1), I values and assignments are summarized in Table I. Outer MO’s can be considered as the appropriate orbitals of the anisole and thioanisole stabilized by the inductive effect of the carbonyl group. The nπ* ionization of the carbonyl group appears in the initial part of the spectrum partly overlapping that of the π(A) orbital (Table I). It should be mentioned that the difference between the experimental and HAM/3 theoretical data of chromone derivatives is higher (±0.3 – 0.4 eV) than in the case of the planar chromones. The CNDO/S method provided similar results (±0.5 eV) for the sulfur-containing compounds. The reasons for this may be the flexible structure of the chromone derivatives, viz. the AM1 optimized geometries are approximately valid only. In the case of 2a and 2d, for the first three π MO’s 0.2 – 0.3 eV stabilization was observed in comparison with the anisole and thioanisole.

HOMO of the acetonophene π(b1) is more stable by 0.15 eV than that of the benzene which is less than the 0.3 eV stabilization appearing at the π orbital π(a). In the former case, this is in accordance with the equilibrium of the -I and +M effects while the -I effect predominates in the latter. For compounds 2a and 2d, higher stability of the HOMO [π(A)] in comparison with the π(A) at 9.44 eV can be evaluated by the decrease of the conjugation originating from the decreasing planarity. This is corroborated by other data, e.g. the enhanced nπ*I values of compounds 3a and 3i if compared with substances 2a and 2b (Table I). In the case of compound 2a and probably 2d, where the ring C has no aromatic character, in comparison with 3a and 1a, a considerable decrease of the donor (–O–) and acceptor (O =) interaction is confirmed by the XPS data, as well. Two O 1s peaks are observed in the XPS spectra, viz. that of the carbonyl oxygen at a higher eV value and the other belonging to the O 1s.
ionization of the ethereal oxygen at a lower eV value. They are 531.4 eV and 534.5 eV for the chromone (3a) and 531.6 eV and 535.0 eV, respectively, in the case of γ-pyronone (1a). The difference of these peaks depends on the polarization of the molecule. The difference decreases as follows: compound 1a (3.4 eV) $>$ 3a (3.1 eV) $>$ xanthone (2.9 eV) $>$ substance 2a (1.3 eV), indicating that the polarization is decreased by the annellation. On the other hand, this order proves that the decrease of the planarity in the case of 2a, in comparison with 3a, is manifested in the dramatic decrease of the conjugation. It is worth mentioning that this holds for the case of flavanone (2b) and flavone (3b) and their thio analogues, respectively, as well. Compounds 2b, 2e, 3b and 3d – 3f can be considered as the 2-phenyl derivatives of 2a, 2d, 3a and 3j – 3k. Their HeI PES are shown in Figure 4 and some selected l values and the assignment are summarized in Table I. The interaction diagram of flavone (3b) and the HAM/3 results are shown in Figure 1. The replacement of the hydrogen by a phenyl group at position 2 (compounds 2b and 2e) resulted in the appearance of two new bands in the low energy region, viz. 9.1 eV [$\pi$(Ph)] and 9.5 eV [$\pi$(Ph)] (Table I). This is in accordance with the splitting of the $\pi$(e$_{1g}$) MO of the benzene in its alkyl derivatives and with the stabilization originating from the inductive effect of the heterocyclic ring. According to the PMO theory, the MO’s of the flavone (3b) can be derived from the appropriate orbitals of the benzene and chromone (3a) (Figure 5). However, the PE spectra of chromone (3a) and flavone (3b) are considerably different. As indicated by the HAM/3 data (Figure 5), the phenyl group at position 2 is a part of the

Figure 4. HeI PE spectra (low-energy regions) of flavanone (2b), 1-thioflavanone (2e), flavone (3b), 1-thioflavone (3d), 4-thioflavone (3e) and 12,4-dithioflavone (3f).
Figure 5. Experimental and theoretical UPS data and the PMO interaction diagram of flavone
(3b) (○ positive, ● negative).
conjugate system. Highest \( \pi \) MO's of compound 3a and 3i - 3k have coefficients different from zero. The interaction of the \( \pi(\text{Ph}) \) orbital, which is a symmetric component of the benzene-like \( \pi(e_{1g}) \) MO, with these results not only in the appearance of two new bands in the case of compounds 3b and 3d - 3f but the energy difference between the HOMO \( \pi(C) \) and \( \pi(C, \text{Ph}) \) orbitals enhances as well. This energy enhancement is 0.3 eV for the carbonyl compounds, 0.6 - 0.7 eV for the thiocarbonyl derivatives but the \( \pi(\text{A}, \text{Ph}) \) orbital is practically unaltered. These relatively small effects can be evaluated by the lack of the planarity and by the small values of the wave function coefficients at the C-2 atom. The character and localization of the HOMO level of compounds with C-2 phenyl group is similar to the appropriate chromone derivatives. In the case of flavone (3b) and 1-thioflavone (3d), the increase of delocalization, in comparison with chromone (3a) and 1-thiochromone (3i), is indicated by the lower \( n_{\sigma} \) ionization energies which are in accordance with the lower IR carbonyl stretching frequencies. \( \nu_{\text{C}=\text{O}} \) (CCl\(_4\), cm\(^{-1}\)) are 1655 (chromone; 3a), 1647 (flavone; 3b), 1640 (1-thiochromone; 3i), and 1629 (1-thioflavone; 3d). In comparison with the chromone (3a), a more pronounced aromatic character of the heterocyclic ring of flavone (3b) is corroborated by the lower ionization energy (by approx. 3 eV) of the \( n \) electron pair of the ethereal oxygen (Figure 5).

PE spectra and \( J \) values of flavone (2b) and isoflavone (2c) are very similar, as expected from the low interaction between the phenyl group at position 2 or 3 and the heterocyclic ring (Table I). While the spectra of flavone (3b) and isoflavone (3c) are characteristically different (Figure 6). In the case of isoflavone (3c), there is a weaker interaction between the phenyl group at C-3 and the chromone skeleton, as shown by the HAM/3 results in accordance with our previous studies\(^2\) as well. HOMO is mainly a \( \pi \) orbital localized on the phenyl moiety at position 3 and on ring C. The less aromatic character of ring C is reflected in higher \( n_{\sigma} \) and \( n_{\pi} \) ionization energies in comparison with flavone (3b). In the case of \( \pi \) orbitals, originated from the aromatic rings between 9 - 10 eV, the expected shifts were observed, e.g. the \( \pi(\text{Ph}) \) level of flavone (3b) is more stable than that of isoflavone (3c). At the same time, however, in the case of flavone (3c) (Figure 5), the \( \pi(C) \) orbital (flavone 10.42 eV and isoflavone 10.21 eV) localized on the whole chromone skeleton has a character extended to the phenyl group at position 2 which is absent in isoflavone (3c) (Figure 6). Oxidation of the sulfur atom of compound 2e results in the formation of a sulfoxide (2f) which is reflected in the PE spectrum (Figure 7) in an approx. 0.6 eV shift of the bands and in the appearance of a new band at 10.33 eV. This new band originates from the ionization of the \( \pi_{\text{sd}} \) MO in accordance with the 10.1 - 10.3 eV literature data of the alkyl and aryl sulfoxide.\(^{11,12}\) It should be mentioned that, although the CNDO/S method did not provide good results as far as the data are concerned, the character of the orbitals of the sulfoxides and sulfones was well-reflected, as checked by a comparison with simple molecules, e.g. methyl phenyl sulfoxide and methyl phenyl sulfone.\(^{11,44}\) Oxidation of the 1-thioflavanone (2e) to its sulfoxide (2f) resulted in a weak destabilization of the \( n_{\sigma} \) orbital (Table I). Owing to the inductive effect of the oxygen atom, in the case of the 1-thioflavone (3d) and its sulfoxide (3g) the S \( \rightarrow \) SO transition should result in orbital stabilization. Results of the optimization of the geometry by AM1 method reveal that the sulfoxide moiety and the phenyl group at C-2 are in spatial proximity. The distance between the oxygen atom and the phenyl group is approx. 2.3 pm and such a spatial effect should, therefore, be taken into consideration, which is absent in the appropriate flavone derivatives owing to their quasiplanar arrange-
Figure 6. HeI UPS data experimental and the HAM/3 and PMO interaction diagram of isoflavone (3e) (○ positive, ● negative).
Figure 7. Low-energy regions of the HeI PE spectra of 1-thioflavanone-1-oxide (2f), 1-thioflavanone-1,1-dioxide (2g), 1-thioflavone-1-oxide (3g).

ment. More pronounced changes have been found on the oxidation of the 1-thioflavanone-1-oxide (2f) to 1-thioflavanone-1,1-dioxide (2g) (Figure 7). MO’s are more stable in the sulfone. On the basis of the data of the methyl phenyl sulfone, it can be concluded that the carbonyl group of the 1-thioflavanone is almost without influence on the SO₂ moiety and, therefore, the $\pi_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ orbitals appear at 11.0 eV and 11.68 eV, respectively, which is almost the same as the appropriate data of the methyl phenyl sulfone. Stabilization of the MO’s belonging to the aromatic rings is a consequence of the high $\pi$ effect of the SO₂ group (Table I). In comparison with compound 3g, in the case of 3h, a stabilization of the HOMO was observed, which is in agreement with the general findings. The extent of the inner $\pi$ MO’s is modified in the sulfone if compared with the appropriate thioether, since the $\pi$ orbital of the SO₂ group appears at 10.5 – 12 eV. In the spectrum, a band is found at 10.7 eV, which is a $\pi$ orbital localized on the SO₂ group. A band at 11.86 eV originates from two neighbouring degenerated MO’s ($\pi + \sigma$) localized on the SO₂ group. In the case of the diphenyl sulfone, this band appears at 11.74 eV.

CONCLUSIONS

In our present paper, HeI PES data of chromanone and chromone derivatives and their thio analogues, respectively, have been evaluated by means of the PMO theory and various semiempirical quantumchemical calculations, viz. the HAM/3, CNDO/S and AM1 methods. MO’s of the appropriate molecules have been assigned and the reflection of the structural changes has been evaluated. It has been found that the
HAM/3 method, along with the AM1 geometry optimization, provides excellent results. The CNDO/S method, though it gives acceptable results as far as the character of the orbitals is concerned in the case of the sulfoxide and sulfones, is not satisfactory for the evaluation of the UPS data.

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SAŽETAK

He(I) fotoelektronski spektri flavonoida i tioflavonoida. II.
Fotoelektronski spekttri derivata kromona i 1-tiokromona

Zoltán Dinya, Ferenc Sztericskai, Albert Lévai i György Litkei

Snimljeni su He(I) fotoelektronski spektri nekih derivata kromanona i kromona kao i niza njihovih tio-analoga. Spekttri su interpretirani usporedom izmjerjenih energija ionizacije s energijama najviših popunjenih molekulskih orbitala (MO) izračunatih semiempirijskim metodama HAM/3 i CNDO/S i primjenom perturbacijskoga MO postupka.