# Heterocycles. XIII. N1s Orbital Binding Energies of Some Quinazolines and Pyrimidines by XPS

N. R. El-Rayyes*, A. Katrib, F. M. Al-Kharafi and B. D. El-Issa

Department of Chemistry, Kuwait University,
Kuwait

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The X-ray photoelectron spectra of some quinazolin-2(1*H*)-ones **IIa,b**, show only one relatively symmetrical line in the N1s binding-energy region, where as the corresponding dehydrogenated products **IIIa,b** and the pyrimidin-2-(1*H*)-ones **Va,b** revealed two well-resolved spectral lines with an energy difference of more than 1 eV. However, compounds **IIc** and **IIIc** gave only one broad unsymmetrical line.

Quantum mechanical calculations on compounds **IIa** and **IIIa** as well as analogues **IIc** and **IIIc** supported the experimental findings.

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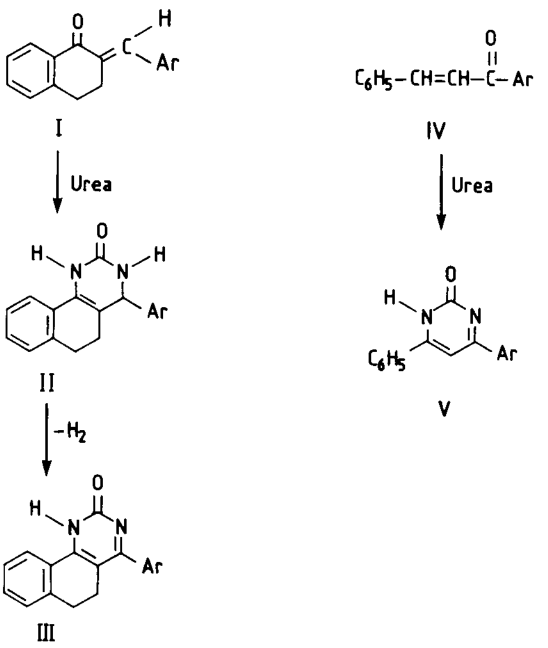
It has been shown that X-ray photoelectron spectroscopy is a powerful tool in establishing the structure of some organic compounds [1,2]. Previous X-ray photoelectron studies on some nitrogen containing compounds revealed the differentiation between them on the basis of the nitrogen 1s orbitals [3-5].

The present work records an investigation of the N1s binding energies of the nitrogens of 4-arylbenzo[*h*]hexahydroquinazolin-2(1*H*)-ones **IIa-c** and their dehydrogenation products 4-arylbenzo[*h*]tetrahydroquinazoline-2(1*H*)-ones **IIIa-c**, in addition to 4-aryl-6-phenyl-pyrimidin-2(1*H*)-ones **Va,b**, using X-ray photoelectron spectroscopy.

Experimental results revealed that the N1s binding-energy region for compounds **IIa,b** (*cf.* Scheme 1) show the presence of one relatively symmetrical line (*cf.* Table 1, Figure 1). On the other hand, the X-ray photoelectron spectra of compounds **IIIa,b**, obtained by dehydrogenation of **IIa,b**, revealed two spectral lines in the N1s binding energy regions. These differ by more than one electron volt, depending on the nature of the aryl substituent at position 4 (*cf.* Figure 2). The same behaviour was also shown by compounds **Va,b** (*cf.* Table 1).

Scheme 1



| Compound | Ar | Compound | Ar |
|---|---|---|---|
| I-III a | $C_6H_5$ | V a | $C_6H_5$ |
| b | $2\text{-}C_4H_3S$ | b | $p\text{-}Br\text{-}C_6H_4$ |
| c | $p\text{-}Cl\text{-}C_6H_4$ | | |

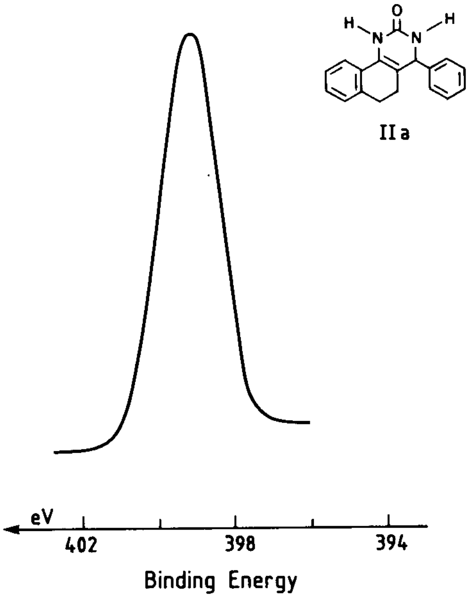


Fig. 1 : The N (1s) Binding energy region of IIa .

The experimental results of compounds **IIa,b** indicate that the 1s electrons of the two nitrogens of these compounds have the same electronic environment and accordingly the same binding energies. This can be explained on the premise that the two electron pairs of the nitrogen

Table 1

N1s Binding Energies (eV) of Compounds **II**, **III** and **V**

| Compound | Found | | ΔE | Calculated | | ΔE |
|---|---|---|---|---|---|---|
| | N-3 | N-1 | | N-3 | N-1 | |
| **IIa** | 399.6 | | – | 398.06 | 398.22 | 0.16 |
| **b** | 4.00.0 | | – | | | |
| **c** | 399.9 | | – | 397.9 | 398.03 | 0.13 |
| **IIIa** | 397.9 | 399.5 | 1.6 | 394.08 | 396.22 | 2.14 |
| **b** | 397.5 | 399.5 | 2.0 | | | |
| **c** | 398.6 | – | – | 393.9 | 395.9 | 2.0 |
| **Va** | 398.4 | 400.1 | 1.7 | | | |
| **b** | 398.8 | 400.1 | 1.3 | | | |

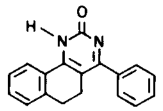
atoms do not interact considerably with the adjacent carbon atoms; resulting in the observation of only one relatively symmetrical line in the N1s region.

The occurrence of two spectral lines in the N1s energy region of compounds **IIIa,b** and **Va,b** may be explained on the premise that the lone pair of electrons of the amine nitrogen (N-1) of these compounds will be involved in bonding with the adjacent carbon. This results in an increase in the effective nuclear charge attraction on the 1s electron, thus increasing its binding energy as compared to the 1s of the imine nitrogen (N-3). It is noteworthy to mention at this respect that the conjugation of the lone pair of N-1 with adjacent double bonds in pyrimidine systems was previously indicated by X-ray diffraction studies [6].

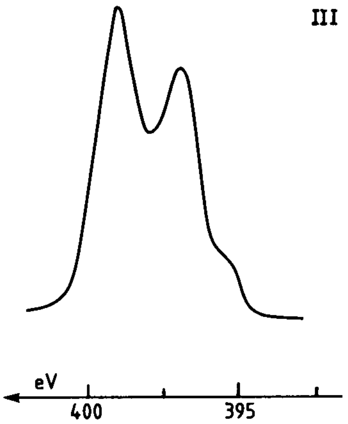
In order to substantiate the above experimental findings, quantum mechanical calculations were accomplished on compounds **IIa** and **IIIa** and analogues of compounds **IIc** and **IIIc**. The method used was HAM/3 [7-9] which has been successfully applied on organic compounds of a similar nature [10]. The value of the method rests in the fact that it can predict ESCA energies by a method that involves subtracting the heat of formation when a core level electron has been removed. In opting for this particular method, standard bond lengths and angles of similar compounds were used [11], and our interest was mainly directed towards trying to establish whether the N1s ESCA energies are dependent on the $\pi$-electron density.

The HAM/3 results were in good agreement with the experimental data and indicate that the binding energies of the N1s orbitals are very close to each other in compound **IIa,** whereas in compound **IIIa** these energies are predicted to be 396.22 eV for the amine and 394.08 eV for the imine nitrogens (*cf.* Table 1). This constitutes a difference of 2.14 eV as compared to the experimental difference of 1.6 eV, and the agreement of the position of the peaks and their assignment is seen to correlate very well in the two sets of results.

The difference in the N1s binding energies of the amine and imine nitrogens of compound **IIIa** was also predicted by calculating their effective formal charge. Thus the net charge of the amine (N-1) nitrogen was found to be +1.01 e⁻ as compared to a net charge of -0.02 e⁻ on the imine nitrogen (N-3). Accordingly, the binding energy of the 1s electron of N-1 is expected to be higher than that of N-3. This is consistent with the experimental and theoretical ESCA energies of the two nitrogens.



III a



Binding Energy

Fig. 2 : The N (1s) Binding energy region of IIIa .

The XPS of the pyrimidine systems **III** and **V** seems to be affected by the presence of a halogen atom at the para-position of the phenyl substituent at position 4. Thus, compound **IIc** showed, in the N1s energy region, a broad unsymmetrical line, which peaks at 399.9 eV. The spectral line of its dehydrogenation product **IIIc**, (Ar = $p$-Cl-$C_6H_4$) was still broader. Furthermore, compound **Vb** (Ar = $p$-Br-$C_6H_4$) showed smaller binding energy difference (1.3 eV) as compared to 1.7 eV for compound **Va** (Ar = $C_6H_5$).

In order to establish the effect of the halo-substituent, a calculation of the fluoro analogues of **IIc** and **IIIc** was accomplished. It is unfortunate that the present version of the HAM/3 method cannot undertake calculations for the chloro- or bromo-analogues.

Theoretical calculations revealed that the N1s binding energies of the two nitrogens in the fluoro analogue of **IIc** are very close to each other. However, in case of the fluoro analogue of **IIIc** these energies were found to be 393.9 eV and 395.9 eV for the imine and amine nitrogens respectively. The difference between these values is 2.0 eV as compared to 2.14 eV in the halogen free analogue **IIIa**.

It can be argued in this respect that the presence of the halogen atom results in a smaller difference of the N1s binding energies as compared to non-halogenated analogues. This can be ascribed to the presence of long-range interaction between the non-bonding *p*-electrons of the halogen atom and the imine lone pair of electrons. This results in a relative increase in the binding energy of the imine N1s electrons, thus becoming closer to that of the amine N1s electrons.

## EXPERIMENTAL

The X-ray photoelectron spectra were measured using a McPherson ESCA-36 spectrometer with an Mg Kα source (1253.6 eV). A cryogenic pump maintained a pressure in the sample chamber less than $10^{-8}$ torr. Samples were mounted on aluminium mesh; their temperatures were approximately ambient. The spectral data were computer-processed to reduce instrumental broadening of the peaks.

The preparation of the quinazolines **II**, **III** and the pyrimidines **V** was previously described [12,13].

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