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# Photoelectron spectroscopy of quinoline derivatives. Correlation of experimental ionization potentials with calculated molecular energies

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## Abstract

Experimental ionization potentials of quinoline **1** and substituted quinolines: 6-methylquinoline **2**, 2,6-dimethylquinoline **3**, 6-methoxyquinoline **4**, 3-bromoquinoline **5**, 2-chloro-4-methylquinoline **6**, 4-hydroxyquinoline **7**, 4-hydroxy-2-methylquinoline **8**, 2-hydroxy-4-methylquinoline **9**, 4-methoxyquinoline **10**, 4- methoxy-2-methylquinoline **11**, 2-methoxy-4-methylquinoline **12**, were measured by photoelectron spectroscopy. Molecular orbital energies of the same derivatives were calculated by the Austin Method 1. The assignments of the bands of the photoelectron spectra were done with the aid of the theoretical calculations and on the basis of the substituent effects. For quinolines **1**–**6** a good agreement was found between the experimental ionization potentials and the calculated orbital energies. © 1997 Elsevier Science B.V.

*Keywords:* Ionization potentials; Molecular energies; Photoelectron spectroscopy; Quinolines

## 1. Introduction

The development of photoelectron spectroscopy (PES) has made possible the direct experimental study of many chemical problems. In particular, the comparison of the photoelectron spectra with the molecular orbital calculations is an interesting tool in the analysis of preferential structures in the gas phase. Molecular orbital calculations produce a list of orbital energies which can be, within the Koopmans' approximation, compared with ionization potentials. There may be some hazard in this procedure which assumes that the ordering of the calculated molecular orbital energies in the neutral and in the ionic states are the same [1]. Heilbronner and Schmetzer [2], however, found an excellent correlation between the ionization energies and the orbital energies of some randomly selected compounds.

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This technique has been used extensively to measure the ionization potentials (IPs) of aromatic compounds and to correlate these IPs with theoretical calculations of n, s and $\pi$ orbital energies [3].

Due to their importance in biology, the properties of molecules containing non-bonding electrons are interesting. In this respect, substituted quinolines are an important class of compounds with chemical and biological applications [4].

Several attempts have been made to study the influence of ring strain on chemical bonding and molecular geometry as well as ionization potentials of nitrogen heterocycles [5–8]. There are two models for describing the effect of fusion of strained ring to N-heterocyclic ring on the ionization potential of the lone-pair electrons. First, is the induced orbital rehybridization model [9], and second, the bent-bond (deformation) model [10–13]. In the first model, it was proposed that fusion of a strained ring onto an aromatic system induces a rehybridization of the s-orbitals. Such rehybridization would lead to an enhanced s-character of the orbital of the fused atom which bonds to the N atom. To maximize overlap with this new hybrid, the orbital on the N atom would need an increased $\pi$-character. As a consequence, the non-bonding electron pair on the N atom is in an orbital of higher s-character and thus higher ionization energy. In the second model, the ionization potential of the non-bonding electron pair is correlated to the deformation in the geometry caused by fusion of the strained ring. To distinguish between the two models, Moomaw et al. [3] utilized PES and ab initio molecular orbital calculations using electrons PRDDO (Partial Retention of Diatomic Differential Overlap) [14,15]. They measured and compared the ionization potentials of naphthalene and quinoline derivatives. They posited that the lone-pair ionization potential in the strained quinolines is more sensitive to changes in the CNC angles than to changes in the hybridization of the fused aryl carbons. Finally, they found that the bent-bond model with little rehybridization is more consistent with their calculated ionization potentials.

In this study, the calculated molecular orbital energies for quinoline derivatives were used to assign and correlate with the experimental ionization potentials.

The photoelectron spectra of quinoline and isoquinoline have been reported elsewhere [16–18]. Moomaw et al. measured and calculated the values of the ionization potentials of quinoline, 2,3-dimethylquinoline, 2,3-dihydro-1*H*-cyclopenta($\beta$)-quinoline, 6,7-dihydrocyclobuta($\gamma$)quinoline and 1,2-dihydrocyclobuta($\beta$)quinoline. The analysis of the bands in the photoelectron spectra has been made also on the basis of the perfluoro effect [19,20], as well on the basis of molecular orbital calculations [3,17,21].

## 2. Results and discussion

### 2.1. Assignments of the photoelectron spectra of quinolines *1–6*

The ionization potentials (in eV) were calculated within the Austin Method 1 (AM1). The calculated and experimental ionization potentials of quinoline **1** were compared with those published [3]. The agreement between our results and those reported earlier is satisfactory. The ionization energy of the nitrogen lone pair is overestimated because the Koopmans' approximation does not take into account the effect of the electronic reorganization (Table 1).

Quinoline, **1**, whose photoelectron spectrum is shown in Fig. 1, contains three distinct electronic bands in the region below 11 eV. The first band at 8.65 eV has been previously assigned to the $\pi$1-ionization [3]. The second band between 9 and 10

Table 1
Calculations with the AM1 method and experimental values of ionization potentials of quinoline **1** (eV)

| This work | | [3] | | Assignment |
|---|---|---|---|---|
| Exp. | Calc. | Exp. | Calc. | |
| 8.65 | 9.14 | 8.62 | 8.46 | $\pi$-ionization |
| 9.2 | 9.59 | 9.18 | 9.35 | $\pi$-ionization |
| 9.45 | 10.60 | 9.39 | 10.26 | n-ionization |
| 10.70 | 11.28 | 10.63 | 11.23 | $\pi$-ionization |

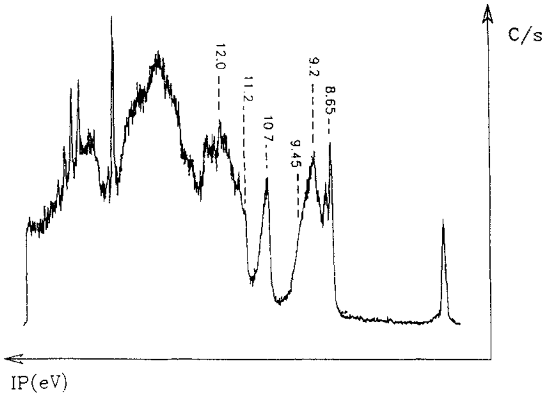

Fig. 1. Photoelectron spectrum of quinoline **1**.

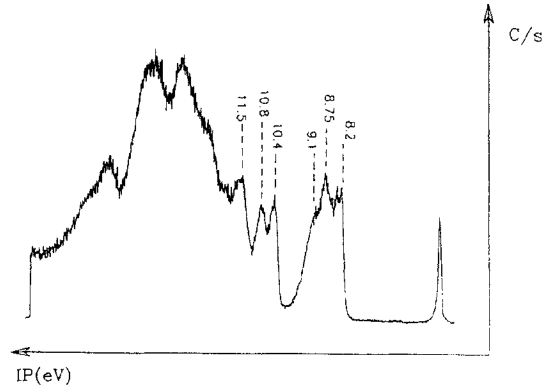

Fig. 3. Photoelectron spectrum of 2,6-dimethylquinoline **3**.

eV is very intense. This strong intensity implies the presence of two ionizations. AM1 calculations support the assignment of the strong feature at 9.2 eV as the π2-ionization and the broad shoulder at 9.45 eV to the lone pair $n_N$-ionization. The higher ionization energy at 10.7 eV corresponds to a $\pi_3$-molecular orbital in our calculations. The photoelectron spectra for quinolines **2** to **4** are virtually identical to the spectrum of quinoline **1** (cf. Figs. 2–4), reserving the same assignment as for the parent compound quinoline **1**. The decrease in ionization potentials for the derivatives **2**, **3**, **4**, is presumably due to the electron-releasing effect of the substituents. This is in good agreement with the calculated molecular orbital energies (Table 2). The electron-releasing groups for compound **3** lower the IPs by about twice compared with compound **2**. This seems to be consistent with the magnitude of the substituent effect. The shift for compound **4** is an average between the two extremes. Less important shifts are observed for the π3-ionization in these three derivatives. These ionizations correspond to π-molecular orbitals in which the contributions of the substituted carbon atoms are minima. In contrast, the fourth ionization potential is shifted by about 0.4 eV for compound **3** (10.8 eV) relative to quinoline **1** (11.2 eV) and the same is observed for **4** (the band at 10.55–10.75 eV, very intense, is related to two orbitals π3 and π4). For both (**3** and **4**) the ionization potentials at 11.5 eV are due to s-orbitals.

The comparison of the spectrum of quinoline **1**, with that of 3-bromoquinoline **5** (Fig. 5), shows the bands due to the ionization from bromine

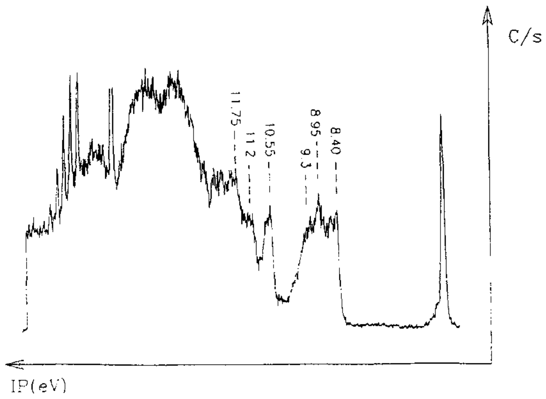

Fig. 2. Photoelectron spectrum of 6-methylquinoline **2**.

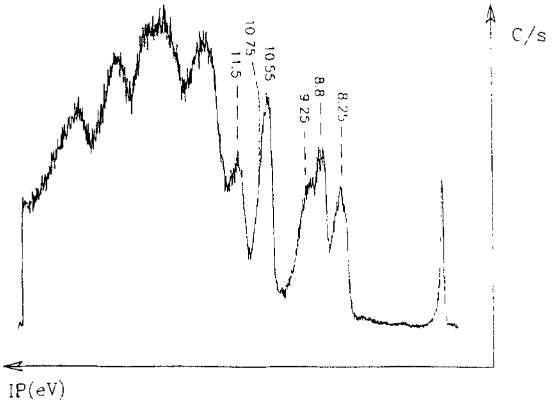

Fig. 4. Photoelectron spectrum of 6-methoxyquinoline **4**.

Table 2
Experimental (PES) and calculated (AM1) ionization potentials (eV) and their assignments for quinoline derivatives **1**–**6**

| Compound | Ionization potential | | Assignment |
|---|---|---|---|
| | Exp. | Calc. | |
| Quinoline **1** | 8.65 | 9.14 | π1 |
| | 9.2 | 9.59 | π2 |
| | 9.45 | 10.60 | $n_N$ |
| | 10.7 | 11.28 | π3 |
| | 11.2 | 12.20 | |
| | 12.0 | 12.50 | |
| 6-Methylquinoline **2** | 8.4 | 9.01 | π1 |
| | 8.95 | 9.36 | π2 |
| | 9.3 | 10.49 | $n_N$ |
| | 10.55 | 11.26 | π3 |
| | 12.0 | 11.2 | |
| 2,6-Dimethylquinoline **3** | 8.20 | 8.93 | π1 |
| | 8.75 | 9.37 | π2 |
| | 9.1 | 10.46 | $n_N$ |
| | 10.4 | 11.20 | π3 |
| | 10.8 | 11.68 | π4 |
| 6-Methoxyquinoline **4** | 8.25 | 8.80 | π1 |
| | 8.8 | 9.53 | π2 |
| | 9.25 | 10.56 | $n_N$ |
| | 10.55 | 11.26 | π3 |
| | 10.75 | 11.59 | π4 |
| 3-Bromoquinoline **5** | 8.7 | 9.35 | π1 |
| | 9.2 | 9.68 | π2 |
| | 9.65 | 10.74 | $n_N$ |
| | a | 11.09 | π3 |
| 2-Chloro-4-methylquinoline **6** | 8.6 | 9.21 | π1 |
| | 9.0 | 9.54 | π2 |
| | 9.7 | 10.76 | $n_N$ |
| | 10.45 | 11.06 | π3 |

[a] Hidden by the bromine ionization.

lone-pairs which appears at 10.5 eV and 10.9 eV. For **5**, the bands observed at 8.7, 9.2, 9.65 and 11.4 eV are assigned, on the basis of theoretical calculations, to $\pi_1$, $\pi_2$, n and $\pi_4$-ionizations, respectively. The $\pi_3$-ionization calculated at 11.23 eV is totally hidden under the bromine ionization. In accord with the calculated orbital energies, these bands are shifted to higher energies relative to those of quinoline **1** (Table 2). This is due to the electron-withdrawing effect of bromine atom.

The assignment of the bands of 2-chloro-4-methylquinoline **6** (Fig. 6) is similar. Therefore, the bands at 8.6, 9.0 and 10.45 eV should correspond to π ionizations. The broad band discerned at 9.7 eV corresponds to $n_N$-ionization. All the π-ionizations are shifted to lower energies (cf. Table 2). In contrast, the n-ionization is shifted to a higher energy value. This may be attributed to the resulting effect of two different types of substituents, the electron-withdrawing chlorine atom and the electron-releasing methyl group. Finally, the ionizations of the chlorine lone pairs correspond to the peaks at 11.00 and 11.2 eV.

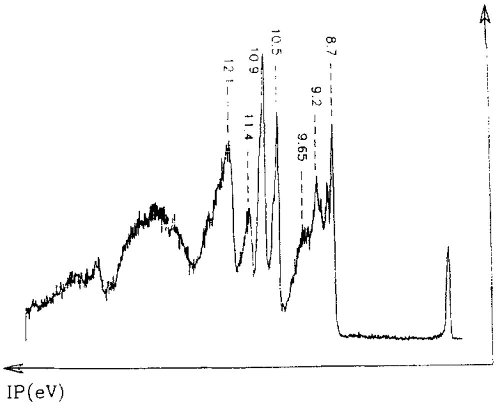

Fig. 5. Photoelectron spectrum of 3-bromoquinoline **5**.

For all these compounds, the ionization of the nitrogen lone pair seems mainly modified by the inductive effect of the substituent in position 2. The calculated geometrical parameters correspond to a close hybridization for the nitrogen atom.

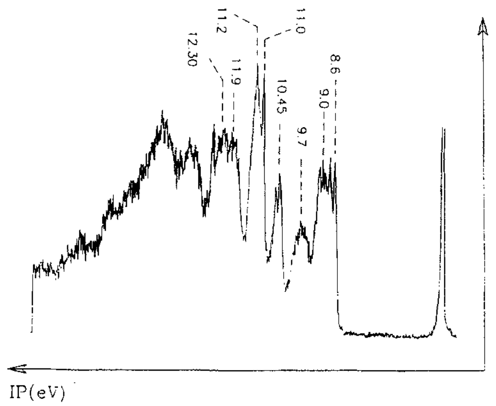

Fig. 6. Photoelectron spectrum of 2-chloro-4-methylquinoline **6**.

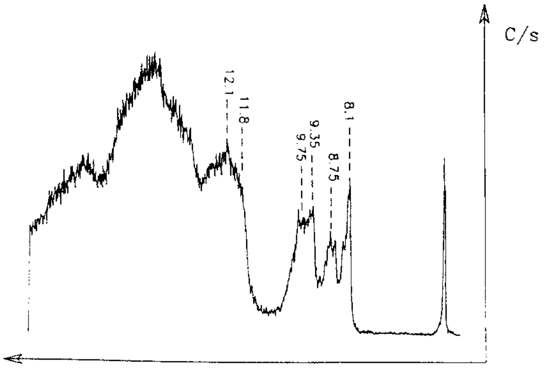

Fig. 7. Photoelectron spectrum of 4-hydroxyquinoline **7**.

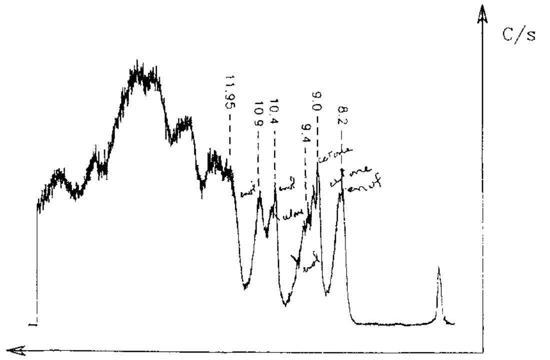

Fig. 9. Photoelectron spectrum of 2-hydroxy-4-methylquinoline **9**.

The CNC angle values are **1**: 117.8; **2**: 117.79; **3**: 118.19; **4**: 117.60; **5**: 118.21; **6**: 117.38.

### 2.2. *Assignments of photoelectron spectra of quinolines 7–12*

The photoelectron spectra of 4-hydroxyquinoline **7**, 4-hydroxy-2-methylquinoline **8** and 2-hydroxy-4-methylquinoline **9** are shown in Figs. 7–9. These PES can be compared with bands obtained for quinoline **1**, 6-methoxyquinoline **4** and the methoxy analogues of hydroxy derivatives 4-methoxyquinoline **10**, 4-methoxy-2-methylquinoline **11** and 2-methoxy-4-methylquinoline **12** (Figs. 10–12).

The experimental values of ionization potentials of **4**, **10**, **11**, **12** are gathered in Table 3. They can be related to the quinoline results. As for 6-methoxyquinoline **4**, the same order $\pi,\pi,n,\pi$ molecular orbitals is observed inside the **10**–**12** series. In each case, the ionization potential assigned to the lone pair of the N atom is not very sensitive to the substituents. The variations are greater for $\pi$ ionizations and may reach 1 eV for $\pi_3$ molecular orbitals (9.7 eV and 9.6 eV) of 4-methoxyquinoline **10** and 4-methoxy-2-methylquinoline **11**. These shifts are related to the sites of substitution and could be expected when the localization of quinoline molecular orbitals is analyzed. The $\pi_3$ orbital is strongly localized on the carbon atom in position 4. As a result, the 10.7 eV value of its ionization potential is strongly lowered (1 eV) in the case of 4-methoxyquinoline **1**.

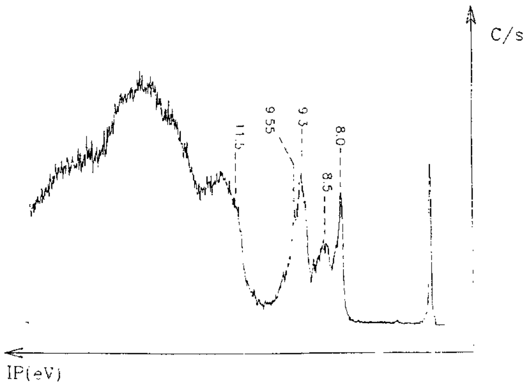

Fig. 8. Photoelectron spectrum of 4-hydroxy-2-methylquinoline **8**.

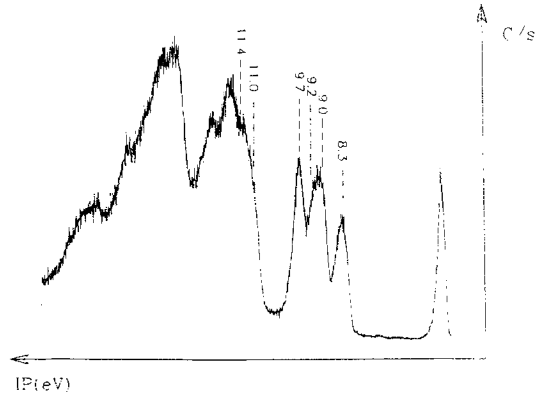

Fig. 10. Photoelectron spectrum of 4-methoxyquinoline **10**.

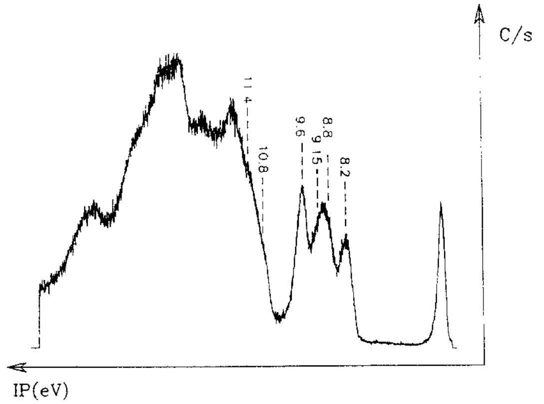

Fig. 11. Photoelectron spectrum of 4-methoxy-2-methylquinoline **11**.

The spectrum of 2-hydroxy-4-methylquinoline **9** (8.2, 9.0, 9.4, 9.6, 10.4, 10.55, 10.9 eV) is more complex. The observed bands do not correspond only to one form. The calculated values of the orbital energy of the enol form **a** and the keto form **b** (see Fig. 13) are close. Then the two forms probably exist in the vapour phase. The first bulky band of the spectrum would correspond to the two mixed ionizations π1 and π2 of the enol form and the first ionization π1 of the keto form. The second broad band with structures at 9.0 and 9.4 eV would be due to the π2 and n0 ionization and at 10.4 and 10.9 to the π3 and π4 orbitals of the enol form. The shoulder at 10.55 eV corresponds to the π3 ionization of the keto form. The temperature variation in the 200°C region, clearly leads to a broadening of the first and second bulky bands on the high energy side. Then the shoulder at 10.55 eV is less pronounced.

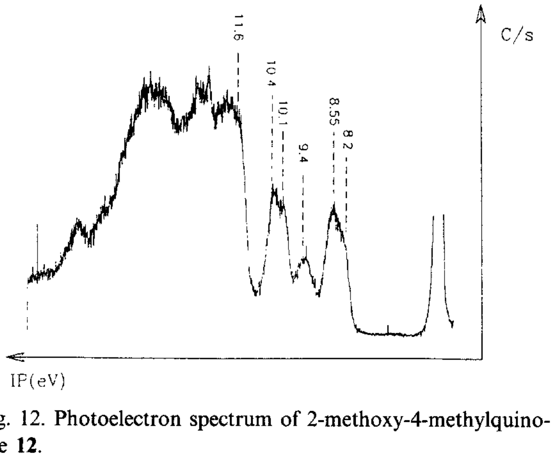

Fig. 12. Photoelectron spectrum of 2-methoxy-4-methylquinoline **12**.

These observations attest to a shift of the equilibrium towards the enol form. As a result, the compound **9** would exist in close amounts of the enol and keto forms. This agrees with the calculated energy of each form. The stabilization value of the keto form is 11.85 kcal.

The 4-hydroxyquinoline compound **7** displays spectroscopic behaviour that is inconsistent with the enol form. If one returns to the calculated orbital energies for the enol form **a** and the keto forms **b**, the spectrum is better understood if the keto form (4-quinolinone) is favoured (Table 4).

The first band (8.1 eV) corresponds to a π ionization. The second one (8.75 eV), showing a possible vibrational structure, can be assigned to the ionization of the lone pair of the oxygen atom. The two bands at 9.35 and 9.75 eV are due to π ionizations. The spectrum of 4-hydroxy-2-methylquinoline **8** is also consistent with the keto form as for the preceding quinoline **7** but in this case the bands lie at 8.0, 8.5, 9.3 and 9.55 eV. The ionization potentials are slightly lowered by the presence of the methyl group. Nevertheless, we cannot exclude a small contribution from the enol form at the temperature and the pressure that we used. We thus observed a shoulder on the high energy side for the first band and a bulky structure in the 9.5 eV region. The calculated energies (Table 4) did not take into account the correlation energy which is known to be differentiated for the systems where the electronic delocalization is not the same. Within these approximations, the calculated energy preference lies near 0.8 kcal for the enol form.

### *2.3. Correlation of experimental and calculated values*

Table 2 contains the experimental ionization potentials and the calculated orbital energies for quinolines **1**–**6**. An exact agreement between the calculated and the experimental values is not, of course, to be expected [16] due to the approximations in the calculation. Nevertheless this study suggests that the highest occupied molecular or-

Table 3
Experimental values of ionization potentials (eV) of quinolines **4**, **10**, **11**, **12**

| Compound | Ionization potentials and assignments | | | | | |
|---|---|---|---|---|---|---|
| **4** | 8.25 $\pi 1$ | 8.8 $\pi 2$ | 9.25 $n_N$ | 10.55 $\pi 3$ | 10.75 $\pi 4$ | 11.5 $\sigma$ |
| **10** | 8.3 $\pi 1$ | 9.0 $\pi 2$ | 9.2 $n_N$ | 9.7 $\pi 3$ | 11.0 $\pi 4$ | 11.4 $\sigma$ |
| **11** | 8.2 $\pi 1$ | 8.8 $\pi 2$ | 9.15 $n_N$ | 9.6 $\pi 3$ | 10.3 $\pi 4$ | 11.4 $\sigma$ |
| **12** | 8.2 $\pi 1$ | 8.55 $\pi 2$ | 9.4 $n_N$ | 10.1 $\pi 3$ | 10.4 $\pi 4$ | 11.6 $\sigma$ |

bital (HOMO) for these molecules is a $\pi$ molecular orbital. Further, the four (five) HOMOs follow the same sequence for the experimental ionization potentials and the calculated molecular orbital energies, i.e. $\pi$, $\pi$, n, $\pi$ (and $\pi$). The $\pi$ donating character in this series increases in the order: 3-bromoquinoline **5** < quinoline **1** < 2-chloro-4-methylquinoline **6** < 6-methylquinoline **2** < 6-methoxy- quinoline **4** < 2,6-dimethylquinoline **3**.

## 3. Conclusions

For all studied quinolines, the calculations as well as the PES indicate that the HOMO is a $\pi$-molecular orbital. Moreover, for substituted quinolines **1**–**6**, the calculated energies of the molecular orbitals and the experimental ionization potentials are of the same order of energy.

The results of the photoelectron spectra suggest that, in the vapour phase, an equilibrium exists between the enol form and the keto form of 4-hydroxyquinoline and 2-hydroxyquinoline. This equilibrium is shifted towards the keto form when the 4 position is substituted. One can underline that the preferred forms are the reverse of the result observed with 4-hydroxypyridine and 2-hydroxypyridine [22]. The annellation induces interactions between the cis diene fragment and the molecular framework leading to higher destabilization for 2- and 4-hydroxyquinoline than for 2- and 4-hydroxypyridine [23]. In the vapour phase, the equilibrium is then shifted to the keto form side.

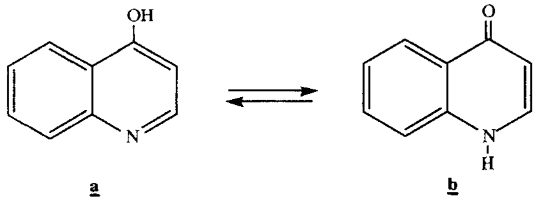

Fig. 13. Protomeric equilibrium of 4-hydroxyquinoline **7**.

## 4. Experimental section

### 4.1. Materials

Quinoline **1**, 6-methylquinoline **2**, and 2-chloro-4-methylquinoline **6** were supplied by Aldrich Chemical Company. 2,6-Dimethylquinoline **3**, 6-methoxyquinoline **4**, 3-bromoquinoline **5**, 4-hydroxyquinoline **7**, 4-hydroxy-2-methylquinoline **8** and 2-hydroxy-4-methylquinoline **9** were obtained from Janssen Company for fine chemicals. 4-Methoxyquinoline **10**, 4-methoxy-2-methylquinoline **11** and 2-methoxy-4-methylquinoline **12** were obtained by treatment of **7**–**9** hydroxy derivatives with excess diazomethane in ether as a solvent for 7 days. In each case, the conversion was not complete and the methoxy derivatives **10**–**12** were separated from the starting hydroxy quinolines **7**–**9** by liquid chromatography on silica gel with anhydrous ether as eluent. After removing the solvent, the structure was confirmed by $^1$H NMR spectroscopy. The purity was checked by CHN analysis. 4-Methoxyquinoline **10**: $C_{10}H_9NO$, calc. C: 75.45; H: 5.70; N: 8.80; found C: 75.32; H: 5.66; N: 8.91; 4-methoxy-2-methylquinoline **11** $C_{11}H_{11}NO$, calc. C: 76.26; H: 6.40; N: 8.09; found C: 76.05; H: 6.24; N: 8.01; 2-methoxy-4-methylquinoline **12** $C_{11}H_{11}NO$, calc. C: 76.26; H: 6.40; N: 8.09; found C: 76.32; H: 6.45; N: 7.98.

The structure of these substituted quinolines can be summarized as follows:

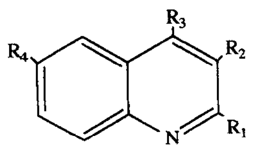

Table 4
Experimental (PES) and calculated (AM1) ionization potentials (eV) and their assignments for hydroxyquinolines **7**–**9**

| Compound[a] | Ionization potentials (calculated) | | | Assignments (exp.) |
|---|---|---|---|---|
| | Enol form (**a**) | Keto form (**b**) | Keto form (**c**) | |
| **7** | 8.96 $\pi 1$ | 8.66 $\pi 1$ | 9.48 $\pi$ | 8.10 $\pi 1$ (**b**) |
| | 9.7 $\pi 2$ | 9.95 $\pi 2$ | 10.07 $\pi$ | 8.75 $n_0$ (**b**) |
| | – | 10.21 $n_0$ | 10.75 $n_0$ | 9.35 $\pi 2$ (**b**) |
| | – | 10.26 $\pi 3$ | 10.89 $n_N$ | 9.75 $\pi 3$ (**b**) |
| | 10.66 $n_N$ | – | – | – |
| | 10.67 $\pi 3$ | – | 12.15 $\pi$ | 11.8 |
| **8** | 8.88 $\pi 1$ | 8.59 $\pi$ | 9.30 $\pi$ | 8.00 $\pi 1$ (**b**) |
| | 9.55 $\pi 2$ | 9.87 $\pi$ | 10.02 $\pi$ | 8.5 $n_0$ (**b**) |
| | 10.59 $n_N$ | 10.06 $\pi$ | – | 9.3 $\pi$ (**b**) |
| | | 10.14 $n_0$ | 10.70 $n_N$ | – |
| | 10.67 $\pi 3$ | – | 10.78 $n_0$ | |
| | 12.02 $\pi 4$ | – | 11.91 $\pi$ | 9.55 $\pi 3$ (**b**) |
| **9** | 8.98 $\pi 1$ | 8.89 $\pi$ | – | 8.0 $\pi 1$ (**b**) |
| | | | | 8.29 $\pi 1$ (**a**) |
| | 9.5 $\pi 2$ | 9.65 $\pi$ | – | 9.0 $\pi 2$ (**b**) |
| | – | – | – | 9.4 n0 (**b**) |
| | 10.65 $n_N$ | 10.89 $n_0$ | – | 9.6 $n_N$ (**a**) |
| | 11.02 $\pi 3$ | 11.15 $\pi$ | – | 10.40 $\pi 2$ (**a**) |
| | 11.80 $\pi 4$ | 11.81 $\pi$ | – | 10.55 $\pi 3$ (**b**) |
| | – | – | | 10.91 $\pi 3$ (**a**) |

[a] 4-Hydroxyquinoline **7**; 4-hydroxy-2-methylquinoline **8**; 2-hydroxy-4-methylquinoline **9**.

**1** $R_1 = R_2 = R_3 = R_4 = H$
**2** $R_1 = R_2 = R_3 = H, R_4 = CH_3$
**3** $R_1 = CH_3, R_2 = R_3 = H, R_4 = CH_3$
**4** $R_1 = R_2 = R_3 = H, R_4 = OCH_3$
**5** $R_1 = R_3 = R_4 = H, R_2 = Br$
**6** $R_1 = Cl, R_2 = R_4 = H, R_3 = CH_3$
**7** $R_1 = R_2 = R_4 = H, R_3 = OH$
**8** $R_1 = CH_3, R_4 = R_2 = H, R_3 = OH$
**9** $R_1 = OH, R_4 = R_2 = H, R_3 = CH_3$
**10** $R_1 = R_2 = H, R_3 = OCH_3, R_4 = H$
**11** $R_1 = CH_3, R_2 = H, R_3 = OCH_3, R_4 = H$
**12** $R_1 = OCH_3, R_2 = H, R_3 = CH_3, R_4 = H$

The photoelectron spectra were recorded on an Helectros 0078 spectrometer using 21.21 HeI radiation as the photon source.

## 5. Computations

The theoretical calculations of the molecular orbital energies were performed using AM1 formalism with the AMPAC set of programs on fully optimized geometries [24,25].

## References

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