Optical absorption measurements and quantum-chemical simulations on 1H-pyrazolo[3,4-b]quinoline derivatives

E. Kościan a, J. Sanetra b, E. Gondek b, A. Danel c, A. Wisła c, A.V. Kityk a,*

a Institute for Computer Science, Technical University of Czestochowa, Armii Krajowej 17, 42-200 Czestochowa, Poland
b Institute of Physics, Technical University of Krakow, Podgorzyszcz 1, 30-084 Krakow, Poland
c Department of Chemistry, Hugon Kollotaj Agricultural University, Al. Mickiewicza 24/28, 30-059 Krakow, Poland

Received 7 June 2003; received in revised form 4 September 2003; accepted 5 September 2003

Abstract

We present the results of experimental studies and quantum chemical simulation (PM3 and AM1 methods) on a new synthesized pyrazolo[3,4-b]quinoline derivatives: 1,4-diphenyl-3-methyl-, 3,4-diphenyl-1-methyl-, 1,3,4-triphenyl-, 1,3-dimethyl-4-phenyl- and 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline. The quantum chemical analysis reveals similarity in the absorption spectra of 1H-pyrazolo[3,4-b]quinoline and 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline which are characterized by four strong absorption bands in the spectral range 200–500 nm. A substitution of the methyl groups by phenyl groups causes substantial changes of the absorption spectra mainly in the spectral range 240–370 nm. We attribute these differences to additional molecular double bonding segments C=C of the substituted phenyl groups i.e., to π→π* transitions. The comparison of measured and calculated absorption spectra by quantum-chemical AM1 method manifests rather good agreement for all compounds in the part regarding the spectral positions of the first oscillator (absorption threshold). At the same time, the measured spectra reveal the considerable broadening practically of all absorption bands. We attribute these discrepancies to a strong solvent effect. By analyzing the charge density distribution we have shown that the most strongest absorption bands in the spectral region 200–270 nm are related with double bonding segments C=N (n→π* transition).

© 2003 Elsevier B.V. All rights reserved.

PACS: 33.20.Lg; 33.20.Kf; 33.70.w

Keywords: Organic materials; Electronic properties; Visible and ultraviolet spectra

1. Introduction

Recent progress in optoelectronics and telecommunications is indebted much to advances in development of new organic molecules and polymers. Due to their technological benefits, organic
materials are being increasingly used for a variety of optical applications including high-density data storage, optical processing, electro-optic modulation and switching, light emitting diodes (LED), displays, sensors and imaging. Among the large number of such materials considerable interest represents 1H-pyrazolo[3,4-b]quinoline and its derivatives which recently have found to be as a class of highly fluorescent materials in the blue spectral range [1] as well as promising materials for electroluminescent applications [2,3], in particular for displays and LED production. Further improvement of their basic characteristics needs a detailed knowledge concerning the fundamental electronic and optical properties of organic molecules implemented into a polymer matrix which currently are not well established. An important information may be gained here by studying of optical absorption in UV and visible parts of the spectra applying appropriate experimental methods and quantum-chemical modeling. Main approach is usually based on the interacting π-electrons which are not only the reason of the optical absorption, but also the basis of the relevant luminescent and electroluminescent properties of materials. Experimental methods itself naturally cannot give all answers regarding the origin of the electronic transitions. Especially this is crucial for organic materials dissolved in solvent or polymer matrix which are known to modify significantly the absorption spectra of organic molecules due to a strong influence of depolarization field.

The general structure of 1H-pyrazolo[3,4-b]quinoline derivatives can be presented by the scheme:

Our previous experiments and quantum-chemical calculations on several pyrazolo[3,4-b]quinoline derivatives, namely with one or two substituted radicals $R_1,R_2 = \text{methyl/phenyl}$, $R_3 = \text{H}$ (called hereafter as group I of derivatives), have revealed that the absorption spectra significantly depends on the pattern of substitution as well as of the type of substituents [4]. A strong modifications of the spectra appeared when at least one phenyl group was introduced what assumed to be related with additional molecular double bonding segments $C═C$, i.e., with $\pi \rightarrow \pi^*$ electronic transitions. At the same time the most strongest absorption bands have been revealed in the spectral region 200–250 nm. The latter ones are found to be related with double bonding segments $C═N$ ($n \rightarrow \pi^*$ transition).

In this paper, we present the results of experiments on a new group of 1H-pyrazolo[3,4-b]quinoline derivatives (called hereafter as group II): 1,4-diphenyl-3-methyl-1H-pyrazolo[3,4-b] quinoline, 3,4-diphenyl-1-methyl-1H-pyrazolo[3,4-b]quinoline, 1,3,4-triphenyl-1H-pyrazolo[3,4-b]quinoline, 1,3-dimethyl-4-phenyl-1H-pyrazolo [3,4-b]quino line and 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline (see chemical structure in optimized geometry, insets in Figs. 1–5). It is amazing, that most of molecules from the group II have no planar configuration. Only 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline is an exception since it, like all derivatives from the group I, possesses by a mirror plane. The experimental results are supplied by quantum-chemical semi-empirical modeling for molecules in vacuum. Dealing with this approach, the quantum PM3- and AM1-method have been found as the most appropriate for simulation of the experimental data in spectral region 200–500 nm.

The main idea behind these simulations is to study how the substituents such as methyl and phenyl influences on the electronic transitions in 1H-pyrazolo[3,4-b]quinoline. One must remember that methyl and phenyl groups is known to contain the bonds with different electronic configuration (namely sp$^3$ and sp$^2$, respectively) which causes the considerable differences in electronic properties of 1H-pyrazolo[3,4-b]quinoline derivatives.

2. Synthesis and experimental

All 4-aryl-1H-pyrazolo[3,4-b]quinoline organic materials used in the study were synthesized following a general procedure known from the literature (see e.g. [5,6]). With some modifications the
The corresponding chemical reaction can be presented by the following scheme:

\[
\begin{align*}
&\text{ArNH}_2 + \text{Cl}\text{C} = \text{N} \rightarrow \text{ArC} = \text{N} \rightarrow \text{ArC} = \text{N} \\
&\text{R}_1 = \text{Me}, \text{Ph} \quad \text{R}_2 = \text{Me}, \text{Ph}
\end{align*}
\]

The following compounds were used in our studies: 1,4-diphenyl-3-methyl-1H-pyrazolo[3,4-b]quinoline [6], 3,4-diphenyl-1-methyl-1H-pyrazolo[3,4-b]quinoline [7], 1,3,4-triphenyl-1H-pyrazolo[3,4-b]quinoline [6], 3,4-diphenyl-1-methyl-1H-pyrazolo[3,4-b]quinoline [7], 1,3,4-triphenyl-1H-pyrazolo[3,4-b]quinoline [7], 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline [8] and 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline [9].

Fig. 1. Measured absorption spectra of 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline (a) and calculated spectra within the semi-empirical quantum chemical PM3 and AM1 models (b). Inset shows the chemical structure of 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline obtained within the geometrical optimization procedure; black balls – N, gray balls – C and white balls – H.

Fig. 2. Measured absorption spectra of 3,4-diphenyl-1-methyl-1H-pyrazolo[3,4-b]quinoline (a) and calculated spectra within the semi-empirical quantum chemical PM3 and AM1 models (b). Inset shows the chemical structure of 3,4-diphenyl-1-methyl-1H-pyrazolo[3,4-b]quinoline obtained within the geometrical optimization procedure; black balls – N, gray balls – C and white balls – H.
Depending on lateral substituents, several described below methods were used for the synthesis of a particular PAQ derivative. In particular, 1,3-dimethyl-4-phenyl-1H-pyrazolo[3,4-b]quinoline was synthesized by Friedländer condensation of 2-aminobenzophenone with 1,3-dimethyl-1H-pyrazol-5-one:

\[
\begin{align*}
\text{NH}_2 & \quad \text{CH}_3 \\
\text{C} & \quad \text{O} \\
\text{NH}_2 & \quad \text{CH}_3
\end{align*}
\]

A mixture of 1,3-dimethyl-pirazol-5-one (0.01 mol) and 2-aminobenzophenone (0.01 mol) was heated in 10 ml ethylene glycol at 180–190 °C for 12 h. After cooling to room temperature the reaction mixture was digested with ethanol (25 ml). The precipitated solid was filtered and dried in the air. The solid was subjected to column chromatography on aluminium oxide using CH2Cl2 as the eluent to afford yellowish crystals in 55% yield, m.p. 164–165 °C. 1H NMR (300 MHz, CDCl3):
A mixture of 1,3-dimethylpirazol-5-one (0.01 mol) and 2-aminoacetophenone (0.01 mol) was heated in 10 ml ethylene glycol at 180–190 °C for 12 h. After cooling to room temperature the reaction mixture was digested with boiling ethanol (25 ml). The precipitated solid was filtered and dried in the air. The solid was subjected to column chromatography on aluminium oxide using CHCl₃ as the eluent to afford yellowish needles in 51% yield, m.p. 142–143 °C. 1H NMR (300 MHz, CDCl₃): δ = 2.71 (s, 3H, 4-Me), 2.83 (s, 3H, 3-Me), 4.07 (s, 3H, 1-Me), 7.34 (t, 1H, H-6, J = 7.55 Hz), 7.66 (t, 1H, H-7, J = 7.61 Hz), 7.97 (t, 2H, H-5, 8, J = 8.67 Hz). Anal. Calcd. for C₁₃H₁₃N₃: C 73.90, H 6.20, N 19.89; found: C 73.81, H 6.16, N 19.75%. The purity of resulted compounds was checked by TLC. The optical absorption spectra were recorded in tetrahydrofuran solution (mass concentration of about 0.1%) using Shimadzu UV-VIS 2101 scanning spectrophotometer in range 200–500 nm. The measurements were performed using standard 1 cm path length quartz cuvette for absorption spectrometry.

3. Calculation procedure

The calculation of optical absorption spectra have been performed using HYPERCHEM computation program (molecular dynamics quantum simulation package). The geometrical optimization has been carried out by (MM+) model (all atom force field model). Together with semi-empirical AM1 and PM3 methods this model is known to be as the most general and frequently used for molecular mechanics calculations developed principally for organic molecules. The calculations of optical absorption spectra were consequently performed within several semi-
empirical quantum chemical models available in this software. However, the results will be presented for AM1 and parameterized PM3 methods, only. It appears that these give the best agreement with the experiment. The electronic transition spectra were calculated considering only the singly excited configuration interactions; the criteria regarding the excitation energies considers either its upper limit of 12 eV (as for PM3-method) or orbital criterion [12 occupied and 12 unoccupied orbitals] (as for AM1-method).

The intensity of absorption bands is determined by the probability $P$ of transition from electronic ground ($j$)- to excited ($k$)-state which are characterized by the energies $E_j = h\omega_j$ and $E_k = h\omega_k$, respectively. In the simplest approximation $P$ is proportional to the density of irradiation $\rho(\omega_{jk})$ and to induced Einstein coefficient $B_{jk}$

$$P = \rho(\omega_{jk})B_{jk}, \quad (1)$$

where the Einstein coefficient is expressed by equation

$$B_{jk} = \frac{8\pi^3}{3h^2} |(\mu)_{jk}|^2. \quad (2)$$

Here, $(\mu)_{jk}$ is a transition dipole momentum described as

$$(\mu)_{jk} = \int \Psi_j^* \nabla \Psi_k dV, \quad (3)$$

where $\Psi_j$ and $\Psi_k^*$ are wave functions of $j$ and $k$ energy levels and $\nabla$ is a transition dipole momentum operator of molecule. The integration is performed over the space volume. The intensity of spectral absorption then reads

$$I(\omega) \approx \omega \sum_{k=1}^{n} \sum_{i=x,y,z} \frac{|\langle \Psi_j^* | \nabla | \Psi_k \rangle |^2}{(\omega - \omega_{jk})^2 + (\Gamma/2)^2}$$

$$= \omega \sum_{k=1}^{n} \sum_{i=x,y,z} \frac{|(\mu)_{jk}|^2}{(\omega - \omega_{jk})^2 + (\Gamma/2)^2}, \quad (4)$$

where $n$ is a number of excited states, $\Gamma$ determines the Lorentzian–Gaussian lineshape broadening; $E_{jk} = h\omega_{jk} = E_j - E_k$ is the transition (excitation) energy from the ground to excited state, $\omega$ is the frequency of incident electromagnetic radiation. Here, the resonance frequencies $\omega_{jk}$ and transition dipole momentum $(\mu)_{jk}$ have been calculated within PM3 and AM1 procedures, as described above. The empirical parameter $\Gamma$ was chosen at reasonable value of 0.12 eV, what gives the best agreement in lineshape of calculated spectra comparing to experimental results.

4. Experimental results and discussion

Measured absorption spectra of 1H-pyrazolo[3,4-b]quinoline derivatives: 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline, 3,4-diphenyl-1-methyl-1H-pyrazolo[3,4-b]quinoline, 1,3,4-triphenyl-1H-pyrazolo[3,4-b]quinoline, 1,3-dimethyl-4-phenyl-1H-pyrazolo[3,4-b]quinoline and 1,4-diphenyl-3-methyl-1H-pyrazolo[3,4-b]quinoline are presented in the Figs. 1(a)–5(a), respectively, whereas the calculated absorption spectra ($\Gamma = 0.12$ eV) are shown in Figs. 1(b)–5(b). One can realize that the spectra of 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline calculated within PM3 (AM1) model is characterized by four relatively strong absorption bands at 400 (390), 261 (252), 244.5 (245.5) and 221.5 (228) nm. It appears to be quite similar to calculated spectra of 1H-pyrazolo[3,4-b]quinoline as well as of several other of its derivatives that contain methyl group only [4]. This fact is quite well understood within basic principles of UV-spectroscopy. Substitution of methyl groups results to additional molecular single bonding segments C–C or C–N only. The optical absorption due to a break of these bonds is related to $\sigma \rightarrow \sigma^*$ transitions which are known to have large energies of excitation. In this case the corresponding absorption bands usually appear in the spectral range <150 nm.

The measured spectra of 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline (Fig. 1(a)) shows also four strong absorption bands at 404, 289.6, 261.6 and 240 nm. The optical gap of 3.07 eV (absorption threshold $\lambda_a = 404$ nm) determined from the experimental data appears to be in fairly good agreement with the quantum chemical simulations which give the magnitude of 3.098 and 3.18 eV as calculated by PM3 and AM1 methods, respectively. Besides these some discrepancies must be
admitted comparing the experimental and calculated spectra. In particular, the absorption band corresponding to the first oscillator looks extreme broad in measured spectra. Other discrepancies arise in the spectral region of 200–300 nm. The positions of three strongest peaks of the measured spectra is shifted here to the region of larger wavelengths by about 15–30 nm, whereas the corresponding absorption bands look rather broad as compared with those obtained by quantum-chemical simulations. What could be the reason for this? The answer on this question might be simply attributed to the possible errors in quantum-chemical methods, but we also cannot exclude a strong influence of the solvent. It must be emphasized that our calculations are done for isolated molecules in vacuum, whereas the measurements were performed on solutions. The absorption spectra of organic molecules in liquid solutions are known to be dependent on the local electric fields generated by the surrounding polar molecules of solvent. Previous spectroscopic studies of liquid solutions show that the absorption wavelength of a solute can undergo both bathochromic (red) and hypsochromic (blue) shifts as the solvent polarity increases [9]. Assuming the observed red shift in tetrahydrofuran solution of 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline to be related indeed with the “solvent effect”, one can then conclude that solvent polarity more strongly stabilize the excited states of molecule comparing to its ground state. Considering that the dipole field decreases as \(1/r^3\) where \(r\) is the distance between the solute molecule and solvent dipoles, only those dipoles nearest the actual molecular segment influences substantially the absorption spectra. Due to molecular thermal motion randomly oriented dipoles would contribute dynamically to blue and red spectral shifts, broadening the overall spectrum. In fact, we clearly observe such broadening for all 1H-pyrazolo[3,4-b]quinoline derivatives (see Figs. 1(a)–5(a)).

A substitution of the methyl groups by at least one phenyl group (Figs. 2–5) causes the substantial changes of both calculated and measured spectra. Quantum chemistry simulations reveals several additional absorption bands in the spectral range 240–370 nm. There is a clear correlation between the intensities of these bands and the number of substituted phenyl groups. Must legibly they are observed in 1,3,4-triphenyl-1H-pyrazolo[3,4-b]quinoline (see Fig. 3(b)) that contains three such groups, whereas in 1,3-dimethyl-4-phenyl-1H-pyrazolo[3,4-b]quinoline most of these bands are rather weak (see Fig. 4(b)). An appropriate interpretation of this naturally refers to additional molecular double bounding segments C=C of the substituted phenyl groups. The corresponding absorption bands may be attributed to \(\pi \rightarrow \pi^*\) electronic transition from the bonding to anti-bounding molecular configuration.

Total spectra of 1,3,4-triphenyl-1H-pyrazolo[3,4-b]quinoline (Fig. 3(b)) contains nine relatively intense bands: 444 (392.5), 351.5 (351), 334 (321.5), 293.5 (290), 278 (277), 269.5 (256), 248 (247.5) 227 (239) and 218.5 (223) nm as calculated by PM3 (AM1) methods. One can see that both calculated spectra show relatively good agreement mainly in the region 200–280 nm, whereas a substantial discrepancy arises in the red region of spectra, namely in the spectral position of absorption threshold. In this case the optical gap calculated using the quantum-chemical AM1 method \(E_g \approx 3.15\) eV give the best agreement with experimental data \(E_g \approx 3.10\) eV. For comparison the quantum-chemical PM3 method give \(E_g \approx 2.79\) eV. The measured spectra of 1,3,4-triphenyl-1H-pyrazolo[3,4-b]quinoline (Fig. 3(a)) possesses by only five resolved spectral peaks at 399, 329, 315, 289 and 254 nm. A broad shape of the absorption bands and their red spectral shift indicate on rather substantial solvent influence on the electronic properties of this solute.

For the remaining derivatives the quantum-chemical simulations give the following absorption bands as obtained by PM3 (AM1) methods; 3,4-diphenyl-1-methyl-1H-pyrazolo[3,4-b]quinoline (Fig. 2(b)): 420 (397), 351 (354.5), 330.5 (323.5), 289.5 (289), 280 (281), 261 (255), 249.5 (248.5), 227 (226), 218.5 (220) nm [experiment (Fig. 2(a)): 394.4, 327.8, 314.8, 301.4, 253.2 nm]; 1,4-diphenyl-3-methyl-1H-pyrazolo[3,4-b]quinoline (Fig. 5(b)): 410.5 (387), 353 (350), 303 (297), 287 (292), 252.5 (250), 243 (236), 224 (232), 219 (220.5) nm [experiment (Fig. 5(a)): 388, 326.2, 312.4, 301.4, 287, 262, 241.4 nm]; 1,3-dimethyl-4-phenyl-1H-pyraz-
olo[3,4-b]quinoline (Fig. 4(b)): 408 (392), 344.5 (359.5), 282.5 (292.5), 256 (245.5), 241 (239.5), 224.3 (221.5), 217 nm [experiment (Fig. 4(a)): 396.4, 380.2, 324.8, 311.8, 251 nm]. Here we see again, that the calculation by both quantum-chemical methods give similar results mainly in the blue region of the spectra. In its red region one can realize a substantial discrepancies, namely in the spectral position of the first oscillator for these compounds. In all cases AM1 method gives the absorption threshold being in fairly good agreement with experiment. The magnitude of the optical gap: $E_g \approx 3.12, 3.20$ and 3.16 eV for 3,4-diphenyl-1-methyl-, 1,4-diphenyl-3-methyl- and 1,3-dimethyl-4-phenyl-1H-pyrazolo[3,4-b]quinoline, respectively. For comparison, the experiment gives $E_g \approx 3.14, 3.19$ and 3.13 eV, respectively.

An additional information concerning the origin of absorption bands can be obtained by considering the electronic charge density distribution [10]. Fig. 6 shows the total charge density distribution for organic 1H-pyrazolo[3,4-b]quinoline derivatives calculated within AM1-procedure. A sketch of the molecules investigated was chosen in such a manner to ensure the best observation of the electronic charge density gradients.

Fig. 6. Total charge density distribution of 1H-pyrazolo[3,4-b]quinoline derivatives: 1,4-diphenyl-3-methyl-1H-pyrazolo[3,4-b]quinoline (a), 3,4-diphenyl-1-methyl-1H-pyrazolo[3,4-b]quinoline (b), 1,3,4-triphenyl-1H-pyrazolo[3,4-b]quinoline (c), 1,3-dimethyl-4-phenyl-1H-pyrazolo[3,4-b]quinoline (d) and 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline (e).
Regarding to this Fig. 6 actually presents the section of charge density distribution by the mirror plane of the pyrazolo[3,4-b]quinoline complex. We see that the largest gradients appear in the regions of nitrogen atoms for all five molecules. As far the nitrogen atom are concerned, only the double bonding segments C\(^@\)N are expected to contribute into the optical absorption above 200 nm. For this reason, we can relate the strongest absorption bands observed for all molecules in the region 200–270 nm with the electronic n→\(\pi^*\) transitions. Here, we must remember again that the charge density distribution in Fig. 6 is calculated for the molecules in vacuum. The influence of solvent on the charge density gradient may be considerable for both ground and excited states. This indeed leads to blue/red shifts in spectral peaks positions as well as modifies the oscillator strengths and accordingly the intensity of absorption bands.

5. Conclusion

We present here the results of experimental investigations and quantum chemical simulation of absorption spectra on new synthesized pyrazolo[3,4-b]quinoline derivatives: 1,4-diphenyl-3-methyl-, 3,4-diphenyl-1-methyl-, 1,3,4-triphenyl- (C), 1,3-dimethyl-4-phenyl- and 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline. The quantum chemical analysis reveals similarity in the absorption spectra of 1H-pyrazolo[3,4-b]quinoline and 1,3,4-trimethyl-1H-pyrazolo[3,4-b]quinoline which are characterized by four strong absorption bands in the spectral range 200–500 nm. A substitution of the methyl groups by at least one phenyl group causes the substantial changes of the absorption spectra mainly in the spectral range 240–370 nm. The correlation between the number of such groups and the intensities of these absorption bands is revealed. We thereby relate these differences with additional molecular double bonding segments C=C of the substituted phenyl groups; the electronic \(\pi \rightarrow \pi^*\) transitions into the absorption mechanism is being involved. The comparison of measured and calculated absorption spectra by quantum-chemical AM1 method manifests rather
good agreement, namely in the part regarding the spectral positions of the first oscillator (absorption threshold). This differs from the recent results of quantum-chemical calculations performed on other pyrazolo[3,4-b]quinoline derivatives (i.e., for group I) [4] as well as on bispyrazolopyridine derivatives [11] where PM3 method gave a bit better agreement with the experiment. The measured spectra reveal a considerable broadening practically of all absorption bands. We attribute these discrepancies to a strong solvent effect. The calculations of the charge density distribution shows that the most strongest absorption bands observed in the region 200–270 nm are indeed related with double bonding segments C=C (the electronic n→\(\pi^*\) transitions).

Acknowledgements

This work was supported by KBN Grant No. 8-T11-B-075-18.

References