Chemical Physics 370 (2010) 194-200

Contents lists available at ScienceDirect

Chemical Physics



journal homepage: www.elsevier.com/locate/chemphys

Optical absorption measurements and quantum-chemical simulations of optical properties of novel fluoro derivatives of pyrazoloquinoline

M.G. Brik^{a,*}, W. Kuznik^b, E. Gondek^c, I.V. Kityk^d, T. Uchacz^e, P. Szlachcic^e, B. Jarosz^e, K.J. Plucinski^f

^a Institute of Physics, University of Tartu, Riia 142, Tartu 51014, Estonia

^b Chemical Department, Silesian Technological University, Ul. M. Strzody 9, Gliwice, Poland

^c Institute of Physics, Cracow University of Technology, Ul. Podchorażych 1, 30-084, Poland

^d Electrical Engineering Department, Czestochowa University of Technology, Al. Armii Krajowej 17/19, Częstochowa, Poland

^e Department of Chemistry, Hugon Kollataj Agricultural University, Al. Mickiewicza 24/28, 30-059 Cracow, Poland

^f Military University of Technology, Electronics Department, 2 Kaliski Str., Warsaw, Poland

ARTICLE INFO

Article history: Received 10 August 2009 In final form 6 January 2010 Available online 11 January 2010

Keywords: Electronic properties Visible spectra Ultraviolet spectra DFT calculations

ABSTRACT

The results of experimental research and quantum-chemical simulations of the absorption spectra of 1-(4-fluorophenyl)-3,4-diphenyl, 3-(4-fluorophenyl)-1,4-diphenyl, and 4-(4-fluorophenyl)-1,3-diphenylpyrazolo[3,4-*b*] quinoline are presented. Although the fluorine atom is located on different phenyl rings in these molecules, the absorption spectra do not differ significantly. Semi-empirical AM1, PM3 and RM1 methods, as well as *ab initio* ADF code-based calculations were used to optimize geometry, calculate the infrared and visible spectra of the afore mentioned compounds and analyze the molecular orbitals schemes. The results of calculations are in good agreement with the experimental data. It was also demonstrated that the positions of the fluorescence maxima depend significantly on the solvent (contrary to the absorption spectra), in which the molecules are embedded, which allows for manipulating with fluorescence properties of the synthesized molecules by changing the solvent.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Recently considerable attention was paid to organic light emitting materials that could be used in various optoelectronic devices, such as the light emitting diodes (LED), sensors and electroluminescent displays (ELD). Pyrazoloquinoline and its derivatives represent a class of chromophore, which is highly fluorescent in a wide spectral range, from blue to green-yellow, depending upon the substituents [1-6]. These compounds are also promising materials for optoelectronic applications [7,8]. Thus, the problem of understanding of the nature of electronic transitions in these systems, theoretical modeling of their optical properties and search for new materials with optimized characteristics is crucially important, in particularly for the understanding of chemical physics of observed phenomena. Recently several papers dealing with solvatochromic effect and the influence of phenyl ring rotation on the UV-Vis absorption spectra of pyrazologuinoline and some of their derivatives have been published [6,9].

In this paper, we present the results of experimental investigations and theoretical simulations of absorption spectra of novel pyrazoloquinoline derivatives: 1-(4-fluorophenyl)-3,4-di-

* Corresponding author. E-mail address: brik@fi.tartu.ee (M.G. Brik).

0301-0104/\$ - see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.chemphys.2010.01.001

phenyl-1*H*-pyrazolo[3,4-*b*]quinoline, 3-(4-fluorophenyl)-1,4-diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline and 4-(4-fluorophenyl)-1,3diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline, for the sake of brevity hereafter referred to as **3a** (**PQF1**), **3b** (PQF3) and **3c** (PQF4), respectively.

The AM1, PM3 and RM1 semi-empirical computational methods and density functional theory (DFT) calculations (as implemented in the Amsterdam Density Functional code (ADF) [10]) were used to simulate the UV and IR spectra; the results of these calculations are compared with experimental absorption spectra of these molecules in acetonitrile and dichloromethane possessing different polarizabilities. These methods are well known to be reliable for organic molecules properties' simulations.

2. Synthesis and experimental

1*H*-pyrazolo[3,4-*b*]quinolines were prepared either by Friedlander condensation (**3a** and **b**) or three-component reaction (**3c**). In the first case *o*-aminobenzophenone 1 was heated with fluorine substituted 2,5-diphenyl-2,4-dihydropyrazol-3-ones **2a** or **2b**. Three-component reaction involved heating of aniline 4, *p*fluorobenzaldehyde and 2,5-diphenyl-2,4-dihydropyrazol-3-one. The last method is one of the best procedures described for the 1*H*-pyrazolo[3,4-*b*]quinoline synthesis (Fig. 1).





Fig. 1. Schemes of preparation of the studied complexes. Top: ethylene glycol, 180–190 °C, 19 h. Bottom: ethylene glycol, 180–190 °C, 2 h. See the text for all notations.

2.1. 1-(4-Fluorophenyl)-3,4-diphenyl-1H-pirazolo[3,4-b]quinoline (**3a**)

2-Aminobenzophenone **1** (395 mg, 2 mmol) and 1-(4-fluorophenyl)-3-phenyl-2-pyrazoline-5-one **2a** (508 mg, 2 mmol) were stirred with 1.5 g of ethylene glycol for 19 h in 190 °C. Then the reaction mixture was cooled and poured into water. Product was extracted with chloroform (common procedure). The extract was flashed through Al_2O_3 and the solvent was evaporated. Crude product was dissolved in toluene and flashed through Al_2O_3 . The solvent was evaporated and the product was crystallized few times from toluene: petroleum ether to give 317 mg (38%) of desired product as yellow crystalline powder, m.p. 206–207 °C.



Fig. 2. Experimental UV–Vis absorption spectra of PQF1, PQF3 and PQF4 in acetonitrile solvent (mass concentration approximately 0.01%).

¹H NMR (300 MHz, CDCl₃) δ [ppm]: 7.03–7.35 (m, 12H), 7.38 (ddd, *J* = 8.6, 6.7, 1.2 Hz, 1H), 7.76 (ddd, *J* = 8.5, 6.7, 1.5 Hz, 1H), 7.90 (dd, *J* = 8.7, 0.8 Hz, 1H), 8.21 (dd, *J* = 8.7, 0.5 Hz, 1H), 8.53–8.60 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ [ppm]: 115.5, 116.4 (d, ²*J*_{*C*-*F*} = 22.7 Hz), 123.2 (d, ³*J*_{*C*-*F*} = 8.0 Hz), 124.2, 124.9, 127.8, 128.2, 128.3, 128.6, 129.1, 129.7, 131.0, 131.2, 133.1, 135.1, 136.8 (d, ⁴*J*_{*C*-*F*} = 2.6 Hz), 145.5, 147.5, 149.3, 150.8, 161.5 (d, ¹*J*_{*C*-*F*} = 244.4 Hz).

2.2. 1,4-Diphenyl-3-(4-fluorophenyl)-1H-pirazolo[3,4-b]quinoline (**3b**)

2-Aminobenzophenone **1** (1.0 g, 5 mmol) and 1-phenyl-3-(4-fluorophenyl)-2-pyrazoline-5-one **2b** (1.3 g, 5 mmol) were stirred with 3 g of ethylene glycol for 24 h in 190 °C. Then the reaction mixture was cooled slightly, ethanol was added to hot solution and the whole mixture was boiled with ethanol. Then the mixture was cooled, and crude product was filtered off. Crude compound was crystallized few times from toluene to give 831 mg (40%) of desired product as yellow needles, m.p. 216–217 °C.

¹H NMR (300 MHz, CDCl₃) *δ*[ppm]: 7.76 (tt, *J* = 8.8, 2.1 Hz, 2H), 7.07–7.14 (m, 2H), 7.20–7.42 (m, 7H), 7.58 (tt, *J* = 9.0, 1.9 Hz, 2H), 7.77 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.89 (dd, *J* = 8.7, 0.8 Hz, 1H), 8.24 (dd, *J* = 8.7, 0.5 Hz, 1H), 8.59 (dt, *J* = 7.6, 1.0 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) *δ*[ppm]: 114.5 (d, ²*J*_{*C*-*F*} = 21.7 Hz), 114.8, 120.9, 123.5, 124.2, 125.5, 127.0, 128.0, 128.5, 128.7 (d, ⁴*J*_{*C*-*F*} = 3.1 Hz), 129.0, 129.1, 130.3, 130.5, 130.8 (d, ³*J*_{*C*-*F*} = 8.4 Hz), 134.5, 139.8, 144.5, 145.7, 148.6, 150.2, 162.4 (d, ¹*J*_{*C*-*F*} = 247.6 Hz).

2.3. 1,3-Diphenyl-4-(4-fluorophenyl)-1H-pirazolo[3,4-b]quinoline (**3c**)

Aniline **4** (0.93 g, 10 mmol), 4-fluorobenzaldehyde **5** (1.24 g, 10 mmol), 1,3-diphenyl-2-pyrazoline-5-one **2c** (2.36 g, 10 mmol) and 4.5 g of ethylene glycol were placed together in round bottom



Fig. 3. Optimized structures of: 1-(4-fluorophenyl)-3,4-diphenylpyrazoloquinoline (PQF1) (top left); 3-(4-fluorophenyl)-1,4-diphenylpyrazoloquinoline (PQF3) (top right); 4-(4-fluorophenyl)-1,3-diphenylpyrazoloquinoline (PQF4) (bottom). Positions of the fluorine and nitrogen atoms are indicated.



Fig. 4. PQF1 experimental (top panel) and calculated UV–Vis absorption spectra of MM + optimized molecular structure (bottom panel) in different solvents: ACN – acetonitrile solution, CH_2Cl_2 – dichloromethane solution, approximately 0.01%.

flask and refluxed for 2 h. Then the mixture was cooled, ethanol was added, and yellow precipitate was filtered of and washed with



Fig. 5. PQF3 experimental (top panel) and calculated spectra of MM + optimized structure (bottom panel). ACN – acetonitrile solution, CH_2Cl_2 – dichloromethane solution, approximately 0.01%.

ethanol. Crude product was dissolved in chloroform and flashed through Al_2O_3 and the solvent was evaporated. Yellow solid was

Table 1

Spectral positions of absorption maxima (in nm) in the experimental spectra of PQF1, PGF3, and PQF4 compounds. The calculated values are in the RM1, PM3, AM1 rows, and the experimental values – in the CH₂Cl₂ and CAN rows.

PQF1	RM1 PM3 AM1	210 204 207	238 237 233	263 260 257	320 310 306	345 350 335	415 438 405
	CH ₂ Cl ₂ 0.01 g/l ACN 0.015 g/l	212		260 260	316 314	328 328	398 396
PQF3	RM1 PM3 AM1	205 202 198	235 234 231	259 262 265	311 308 300	358 360 350	417 440 408
	CH ₂ Cl ₂ ACN	216		260 260	316 314	328 328	398 396
PQF4	RM1 PM3 AM1	204 201 198		236 235 232	265 260 259	312 303 297	419 442 410
	CH ₂ Cl ₂ ACN	220		262 260	316 316	330 328	398 396



Fig. 6. PQF4 experimental (top panel) and calculated UV–Vis spectra of MM + optimized structure (bottom panel). ACN – acetonitrile solution, CH_2Cl_2 – dichloromethane solution, approximately 0.01%.

crystallized from toluene to give 673 mg (16%) of desired product as yellow needles, m.p. 240–242 $^\circ C.$

¹H NMR (300 MHz, CDCl₃) *δ*[ppm]: 6.93 (tt, *J* = 8.7, 2.1 Hz, 2H), 7.12–7.26 (m, 7H), 7.32 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.40 (ddd, *J* = 8.6, 6.7, 1.2 Hz, 1H), 7.58 (tt, *J* = 8.0, 1.9 Hz, 2H), 7.77 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.87 (dd, *J* = 8.7, 0.8 Hz, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.58–8.62 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) *δ*[ppm]: 115.0 (d, ²*J*_{C-F} = 21.8 Hz), 115.2, 120,9, 123.5, 124.3, 125.5, 126.6, 127.6, 127.8, 129.0, 129.1, 129.2, 130.4, 130.5, 132.1 (d, ³*J*_{C-F} = 8.4 Hz), 132.5, 139.9, 143.3, 148.6, 150.2, 162.9 (d, ¹*J*_{C-F} = 248.6 Hz).

The UV–Vis absorption and fluorescence spectra were recorded in acetonitrile and dichloromethane (HPLC grade) solutions (concentrations approximately 0.001% w/w) in a standard 1 cm path length quartz cell using HP 8452A UV–Vis Diode Array Spectrophotometer in the 190–820 nm range with spectral resolution 1 nm. Experimental fluorescence spectra of the studied samples are shown in Fig. 2. The shape of the spectra and the spectral positions



Fig. 7. Sensitivity of the constants *k* to the PQF1 calculated spectra.

of the fluorescence maxima are very similar; there is only a slight difference in the emission intensities determined by their oscillator strengths.

3. Calculation procedure

The calculations of UV–Vis absorption spectra were performed with HyperChem 8.04 package. The molecular structure was optimized with the MM + force field model, which is known as a widely used reliable method for prediction of molecular structure, especially for organic molecules and polymers [11,12]. After that, the calculations of the IR spectra were performed using the ADF package. Fig. 3 shows optimized configurations for the considered molecules. For the sake of brevity, we do not give here the calculated atomic positions (50 atoms for each of this three molecules would mean a rather lengthy table); they can be available from the authors upon request. The structures are different mainly with respect to the mutual positions of the F and N atoms and their attachments to the phenyl rings. The shortest F-C distance is 1.401 Å for the PQF1 molecule, 1.400 Å for the PQF3 molecule, and 1.398 Å for the PQF4. Distances from the fluorine atom to the three nitrogen atoms are (all in Å): 5.54, 6.332, 6.575 for PQF1; 6.371, 7.662, 9.022 for PQF3, and 7.801, 8.477, 8.495, for POF4.

Parametrized semi-empirical methods AM1, RM1 and PM3 were used to calculate the optical spectra taking into account only the singly excited configuration interactions. The orbital criterion of 12 occupied and 12 un-occupied orbitals was chosen for all the three methods. The relatively new Recife Model 1 (RM1) is a re-parametrized Austin Model 1 (AM1) version. Unlike AM1, RM1 uses optimized parameters and has been proven to give better results than both AM1 and PM3 in many cases [13].

4. Results and discussion

4.1. Optical spectra simulation

Figs. 4–6 show the comparison between the experimental and calculated UV–Vis absorption spectra of pyrazoloquinoline fluoro derivatives. There is practically no significant difference between the UV–Vis absorption spectra of PQF1, PQF3 and PQF4, in spite of the fact that fluorine atom is attached to different phenyl rings in their molecular structures (Fig. 3).

In each spectrum there is a wide spectral peak in the visible spectral range with maximum at approximately 400 nm and several peaks of different intensities in the ultraviolet range, namely two small peaks at 330 and 315 and two higher peaks at 260 and 220 nm. No distinct solvatochromic effect can be observed as the experimental absorption spectra of pyrazoloquinoline derivatives in acetonitrile and dichloromethane are practically identical, which is in accordance with earlier observations [14]. The only difference is that the highest energy peak in dichloromethane spectra (210 nm) is not detected, but this is probably a result of relatively low solvent transparency below 230 nm and nothing should be deduced from any results in the far-UV region of these spectra.

Generally, all the applied semi-empirical methods produced quite satisfactory results: the number of peaks simulated and their spectral positions prevailingly coincide with experimental spectra. However, some significant differences between the AM1, RM1 and PM3-derived spectra were found. The first one is the red shift of the visible range absorption band by approximately 40 nm in all the PM3-calculated spectra (Figs. 4–6, Table 1).

Usually this band is of crucial importance for potential optoelectronic applications of these materials. The failure to predict

Density of states

its location accurately has to be considered as a serious drawback of the PM3 method. AM1 prediction of this band was slightly better than that of RM1, but both were closer to the experimental data (see Figs. 4–6, Table 1).

Fig. 7 shows how choice of fitting constant influences the resultant spectra of RM1 prediction of PQF1 absorption. The graphs are built for low values of the fitting constant k: 0.1 and 0.18. This constant is related to the electron-vibration broadening and for these compounds this constant is comparable with other similar materials. One can see that even such a small difference in the constant's value changes the spectrum significantly. When the 0.18 value is used, the spectral peaks are wider, which resembles more the experimental spectra. On the other hand, as the spectral peaks are wide, they may merge to form a wide spectral band instead of two peaks with distinct maxima (Fig. 6, 300–360 nm).

The calculated DOS diagrams (shown below in Fig. 8) are all very reach in the number of the molecular orbitals and include 292 orbitals in total. Analysis of the calculated excitation spectra allows to assign the excitation peaks and narrow down the number of the orbitals involved into the optical transitions: these are the



Fig. 8. Calculated DOS. From top to bottom: PQF1, PQF3, PQF4. The HOMO level in each case is shown by a vertical arrow. Region of the optical transitions is shown by a brace.



Fig. 9. Molecular orbitals scheme in the PQF1 molecule. The occupied orbitals are shown in black color, and un-occupied – in grey. For the sake of brevity similar diagrams for PQF3 and PQF4 are not shown. Vertical scale is the energy in eV.

nearest neighbors (to the lower and higher energies) of the highest occupied molecular orbital (HOMO).

Fig. 9 shows the overall scheme of the molecular orbitals in PQF1 molecule. It is seen from this diagram, that the lowest un-occupied orbitals consists mainly of the C and H contributions. In the highest un-occupied orbitals the H contribution is replaced by that one of N.

Fluorescence spectra were measured in cyclohexane (CHX, nonpolar solvent) and acetonitrile (ACN, polar solvent) media. PQF1 spectrum (Fig. 10) shows strong solvatochromic shift from 455 to 480 nm, PQF3 – 460–485 nm, and PQF4 – 455–480 nm.



Fig. 10. Fluorescence spectra of studied compounds. See text for further details.

4.2. IR spectra simulation

Since all synthesized molecules consist of 50 atoms, 144 normal vibration modes should form the observed experimentally vibrational spectrum. The calculations of the vibrational spectra were performed after optimizing the geometry of the molecules using the ADF program with LDA potential and DZ basis set. The results of the calculations are shown in Fig. 11 (the tables with the calculated vibrational frequencies and coordinates of the atoms in the optimized structures are not given here for the sake of brevity, but are available from the authors upon request). The overall appearance of the spectra is similar: a low intensity vibration at about 3100 cm⁻¹, and two groups of structured intensive lines at about 750 and 1500 cm⁻¹ (the density of the vibrational states in these regions is very high). However, it should be emphasized that redistribution of the IR bands intensities takes place: for example, intensity of the 1500 cm⁻¹ line is decreased in PQF3 and PQF4, compared with that for PQF1. This can be explained by different positions of the fluorine atom in each of these molecules.

5. Conclusions

In the present paper, we report on the synthesis and spectral studies of three organic molecules: 1-(4-fluorophenyl)-3,4-diphenyl, 3-(4-fluorophenyl)-1,4-diphenyl, and 4-(4-fluorophenyl)-1,3diphenyl-pyrazolo[3,4-*b*]quinoline. The experimental studies of the excitation and emission spectra were supported by theoretical quantum-chemical calculations (both semi-empirical and *ab initio*) of the optimized geometry, excitation spectra, DOS and IR spectra of the compounds. The calculated results include the positions of atoms in the optimized structures, normal vibration frequencies and molecular orbital energies. The fluorescence spectra measurements have shown a profound solvatochromic shift of the lumines-



Fig. 11. Calculated vibrational spectra of PQF1 (top), PQF3 (middle) and PQF4 (bottom) vibrations.

cence maxima, which gives an opportunity of tuning the fluorescence properties of the synthesized molecules in different solvents.

References

- [1] Z. He, G.H.W. Milburn, K.J. Baldwin, D.A. Smith, A. Danel, P. Tomasik, J. Lumin. 86 (2000) 1.
- [2] Z. He, G.H.W. Milburn, A. Danel, A. Puchala, P. Tomasik, D. Rasala, J. Mater. Chem. 7 (1997) 2323.
- [3] S. Calus, E. Gondek, A. Danel, B. Jarosz, M. Pokladko, A.V. Kityk, Mater. Lett. 61 (2007) 3292.
- [4] A. Danel, Z. He, G.H.W. Milburn, P. Tomasik, J. Mater. Chem. 9 (1999) 339.
 [5] Y.T. Tao, E. Balasubramanian, A. Danel, B. Jarosz, P. Tomasik, Appl. Phys. Lett. 77 (2000) 1575.
- [6] E. Koscien, E. Gondek, A.V. Kityk, Opt. Commun. 280 (2007) 95.
- [7] L. Mu, Z. He, J. Wang, G. Hui, Y. Wang, X. Jing, A. Danel, E. Kulig, IEEE Photon. Technol. Lett. 20 (2008) 1781.
- [8] E. Gondek, A. Danel, I.V. Kityk, J. Mater. Sci.: Mater. Electron. 20 (2009) 461.
- [9] S. Całus, E. Gondek, M. Pokladko, E. Kulig, B. Jarosz, A.V. Kityk, Spectrochim.
- Acta A 67 (2007) 1007. [10] G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van
- Gisbergen, J.G. Snijders, T. Ziegler, J. Comput. Chem. 22 (2001) 931. [11] M. Czerwiński, J. Bieleninik, J. Napieralski, I.V. Kityk, J. Kasperczyk, R.I. Mervinskii, Eur. Polym. J. 33 (1997) 1441.
- [12] S.W. Tkaczyk, I.V. Kityk, R. Schiffer, J. Phys. D: Appl. Phys. 35 (2002) 563.
- [13] G.B. Rocha, R.O. Freire, A.M. Simas, J.J. P Stewart, J. Comput. Chem. 27 (2006) 10.
- [14] E. Gondek, E. Koscien, J. Sanetra, A. Danel, A. Wisła, A.V. Kityk, Spectrochim. Acta A 60 (2004) 3101.