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# Optical spectra of some 6-styrylo-1*H*-pyrazolo[3,4-b]quinolines

I. Fuks-Janczarek<sup>a</sup>, E. Gondek<sup>b</sup>, I.V. Kityk<sup>b,\*</sup>, K. Danel<sup>c</sup>, L. Krzemińska<sup>c</sup>, J. Sanetra<sup>b</sup>, B. Kwiecień<sup>c</sup>

<sup>a</sup> Institute of Physics, J. Długosz University of Częstochowa, Al.Armii Krajowej 13/15, Częstochowa, Poland <sup>b</sup> Institute of Physics, Technical University of Cracow, ul.Podchorazych 1, Poland <sup>c</sup> Institute of Chemistry, Agricultural Academy of Cracow, Cracow, Poland

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#### Abstract

It was proposed a method of synthesis several 6-styrylo1-1*H*-pyrazolo[3,4-b]quinolines as promising material for optoelectronics. Particularly, 6-styryl-1,3-diphenyl-1*H*-pyrazolo[3,4-b]quinolines were prepared by Wadsworth–Emmons reaction.

One of advantageous of these materials is stability of their optical spectra versus the possible *cis*- and *trans*-transformation.

Theoretical and experimental studies of optical absorption and photoluminescence excitation spectra for styryloquinolines were done. They show that the AM1 semi-empirical method gives better results compared to other approaches. We have found that the solvents do not play a role in the behavior of the spectra. The backside-substituted groups do not influence substantially the observed optical spectra. © 2005 Elsevier B.V. All rights reserved.

Keywords: 6-styrylo1-1H-pyrazolo[3,4-b]quinolines; Wadsworth-Emmons reaction; Semi-empirical method

# 1. Introduction

Among large number of organic optoelectronic materials considerable interest present 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 [1–4]. These materials are potential candidates for use in optoelectronic devices, optical fibers, photonics, medicine and light emitting diodes.

Semi-empirical methods are grounded on restricted Hartree–Fock approach [5,6]. The most frequently used methods (MNDO, AM1, PM3) are all based on the neglect of differential diatomic overlap (NDDO) integral approximation [5–8]. For the AM1 and PM3, the fitting parameterized procedure is performed by the dipole moments. Particularly AM1 method is fitted to transition dipole momentums. How-

Tel.: +48 601504268; fax: +48 223612228.

ever, principal limitation is related to the presence of aromatic groups. So it is necessary to take into account the influence of fitting parameters on the simulated spectra. For us it is important to compare the spectra obtained by this two methods tom work out recommendations for other similar compounds.

The article is as follows: chemical synthesis of styryloquinolines is given in Section 2. In Section 3, we present calculation procedure, molecular geometry optimization, experimental and theoretical absorption and photoluminescence spectra. Conclusions are presented in Section 4.

#### 2. Experimetnal

#### 2.1. Chemical synthesis

The synthesis of 6-styryl-1,3-diphenyl-1*H*-pyrazolo[3,4-b]quinolines 6-Styryl-1,3-diphenyl-1*H*-pyrazolo[3,4-b]quinolines **4** were prepared according to the sequence of reaction depicted on the Fig. 1.

Thus 6-methyl-1,3-diphenyl-1H-pyrazolo[3,4-b]quinoline was prepared by condensation of p-toluidine with

<sup>\*</sup> Corresponding author at: Solid State Department, Institute of Physics AJD Czestochowa, J. Długosz University of Częstochowa, Al.Armii Krajowej 1315, PL42201 Częstochowa, Poland.

E-mail address: i.kityk@ajd.czest.pl (I.V. Kityk).

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Fig. 1. (a) NBS/CCl<sub>4</sub>; (b) P(OEt)<sub>3</sub>/xylene; (c) ArCHO/NaH.

5-chloro-4-formyl-1,3-diphenylpyrazole according to Brack procedure [9]. **1** was heated in carbon tetrachloride with NBS and AIBN yielding **2** [10]. 6-Bromomethyl derivative **2** was heated with triethylphosphite in xylene for 24 h at 140 °C. The styryl derivaties **4** were prepared from ester **3** and appropriate aldehydes in Wadsworth–Emmons reaction.

# 2.2. (1,3-Diphenyl-1H-pyrazolo[3,4-b]quinolin-6ylmethyl)-diethyl phosphonate **3**

This compound was prepared by reacting 2 (2.07 g, 5 mmol) with triethyl phosphite (0.73 g, 5.5 mmol) in xylene (10 ml) at 90 °C for 24 h. The solvent was removed and the oily residue was chromatographed over silica gel using toluene/ethyl acetate (3:1) as eluent.

Yellow crystals, yield 65%, mp 95.7  $^{\circ}$ C (toluene/hexane). Anal. calcd. for C<sub>27</sub>H<sub>26</sub>N<sub>3</sub>O<sub>3</sub>P: C, 68.78; H, 5.56; N, 8.91. Found: C, 68.81; H, 5.74; N, 8.73.

# 2.3. Synthesis of styryl derivatives 4 —general procedure

Appropriate aldehyde (5 mmol) and sodium hydride (60% in oil, 0.2 g, 5 mmol) were put into a 50 ml round-bottomed flask with anhydrous DME (20 ml). To this mixture compound **3** (2.36 g, 0.005 mol) in 10 ml DME was added dropwise at 0 °C with stirring. The solution was stirred at 70 °C for 24 h. After completion of the reaction, some solvent was removed and water was poured into reaction flask. The precipitate was filtered, dried and was further purified by column chromatography.



Fig. 2. Chemical structure of studied compounds styryloquinolines 1, 2, 3, 4.

#### 2.4. 1,3-Diphenyl-6-[(E)-styryl]-1H-pyrazolo[3,4b]quinoline **4a**

Yellow crystals, yield 71%, mp 204.6 °C (toluene). Anal. calcd. for  $C_{30}H_{21}N_3$ : C, 85.08; H, 5.00; N, 9.92. Found: C, 84.98; H, 4.89; N, 9.67.

# 2.5. 6-[(E)-2-(4-Methylphenyl)-vinyl]-1,3-diphenyl-1Hpyrazolo[3,4-b]quinoline **4b**

Yellow crystals, yield 65%, mp 238.40 °C (toluene). Anal. calcd. for  $C_{31}H_{23}N_3$ : C, 85.10; H, 5.30; N, 9.60. Found: C, 84.87; H, 5.17; N, 9.43.

# 2.6. 6-[(E)-2-(2,4-Dichloro-phenyl)-vinyl]-1,3diphenyl-1H-pyrazolo[3,4-b]quinoline **4c**

Yellow crystals, yield 73%, mp 225.8  $^{\circ}C$  (toluene). Anal. calcd. for  $C_{30}H_{19}Cl_2N_3$ : C, 73.11; H, 3.89; N, 8.53. Found: C, 73.22; H, 3.95; N, 8.45.

### 2.7. 1,3-Diphenyl-6-((E))-2-pyridin-4-yl-vinyl-1Hpyrazolo[3,4-b]quinoline **4d**

Yellow crystals, yield 45%, mp 273.5 °C (toluene). Anal. calcd. for  $C_{29}H_{20}N_4$ : C, 82.05; H, 4.75; N, 13.20. Found: C, 81.86; H, 4.56; N, 13.05.

The general structure of a synthesized styryloquinolines derivate molecule is shown in Fig. 2.

#### 3. Results and discussion

#### 3.1. Calculation procedure

The simulation of optical absorption spectra were performed using AM1, PM3 semi-empirical approaches. Molecular structures of the molecules were optimized by molecular-mechanics force field method (MM+) which is particularly useful for carbon-based systems.

We used the MM+-force field method because:

- It is very fast.
- May be used for large organic molecules.
- It gives simultaneously an information about values of total energy and molecular geometry.

As a criterion of self-consistent convergence during the numerical procedure we have chosen a value of energy gradient to be equal to about 0.01 kcal/mol.

Following the calculated optimized molecular structure quantum chemical calculations were done. Due to the relatively large molecular formula and large amount of aromatic rings we applied the semi-empirical quantum chemical methods. All the semi-empirical methods are fitted by choosing of different forms of parameterization in the overlapping integrals. Usually in semi-empirical methods, these integrals are neglected or parameterized, and only valence shell electrons are considered. The Hamiltonian operator takes the form [5]:

$$\hat{H}_{\text{val}} = \sum_{i=1}^{N_{\text{v}}} \left( -\frac{1}{2} \nabla_i^2 + V(i) \right) + \sum_{i=1}^{N_{\text{v}-1}} \sum_{j=i+1}^{N_{\text{v}}} \frac{1}{r_{ij}}$$
$$= \sum_{i=1}^{N_{\text{v}-1}} \hat{H}_{\text{val}}^{\text{core}}(i) + \sum_{i=1}^{N_{\text{v}-1}} \sum_{j=i+1}^{N_{\text{v}}} \frac{1}{r_{ij}}$$
(1)

where  $N_v$  is total number of valence electrons in the molecule, V(i) the potential energy of the *i*th electron in the field of nuclei and inner-shell electrons.

The AM1 and PM3 methods use Slater-type orbitals (STOs) as basis set functions:

$$f = Nr^{n-1} e^{-\xi r} Y_1^m(\theta \phi)$$
<sup>(2)</sup>

where  $Y_1^m$  is spherical harmonic special functions. As a rule one do the following simplifying approximation:

$$\iint \frac{f_z^*(1)f_y(1)f_m^*(2)f_n(2)}{r_{12}} \,\mathrm{d}\nu_1 \,\mathrm{d}\nu_2 = \delta_{zy}\delta_{nm}(zy|mn) \quad (3)$$

where  $\delta_{zy}$  is Kronecker symbol. The  $F_{yy}$  terms in the secular determinant have a form:

$$F_{yy} = U_{yy} - \sum_{B \neq A} C_B(yy + s_B s_B)$$
  
+ 
$$\sum_{z}^{A} P_{zz} \left[ (yy|zz) - \frac{1}{2} (yz|yz) \right]$$
  
+ 
$$\sum_{B \neq A} \sum_{p}^{B} \sum_{q}^{B} P_{pq}(yy|pq)$$
(4)

where the core integral  $U_{yy}$  is

$$U_{yy} = \left\langle f_y \left| -\frac{1}{2} \nabla^2 + V_A \right| f_y \right\rangle \tag{5}$$

The orbitals  $f_z$  and  $f_y$  are centered on atom A, and orbitals  $f_p$ and  $f_q$  are centered on atom B.  $C_B$  is the core charge on atom B, i.e. atomic number of atom B minus the number of innershell electrons, and  $(yy|s_Bs_B)$  is a two-electron, two-center overlapping integral. The  $s_B$  orbital is the valence s orbital on atom B.  $P_{zz}$  and  $P_{pq}$  are called density matrix elements and are defined as

$$P_{zz} \equiv 2 \sum_{j=1}^{(1/2)N_{\rm v}} c_{zj}^* c_{zj} \tag{6a}$$

$$P_{pq} \equiv 2 \sum_{j=1}^{(1/2)N_{v}} c_{pj}^{*} c_{pj}$$
(6b)

for closed-shell configurations. There are two types of possible presentation of the off-diagonal elements  $F_{zy}$  in the secular determinant. The element in which the  $f_z$  and  $f_y$  orbitals are on the same atom constitutes one type and is

labeled  $F_{zy}^{AA}$ . The other type of off-diagonal element has the  $f_z$  and  $f_p$  orbitals on different atoms and is labeled  $F_{zp}^{AB}$ .

$$F_{zy}^{AA} = -\sum_{B \neq A} C_B(zy|s_B s_B) + \frac{1}{2} P_{zz}[3(zy|zy) - (zz|yy)] + \sum_{B \neq A} \sum_p^B \sum_q^B P_{pq}(zy|pq)$$
(7a)

$$F_{zp}^{AB} = \frac{1}{2} [\beta_z + \beta_p] S_{zp} - \frac{1}{2} \sum_{y}^{A} \sum_{q}^{B} P_{yq}(zy|pq)$$
(7b)

 $S_{zp}$  is the overlap integral  $\langle f_z | f_p \rangle$  and it is calculated exactly. The total energy of the molecule,  $E_{\text{total}}$ , is the sum of the total valence electronic energy,  $E_{\text{el}}$ , and the energy of repulsion between the cores on atoms *A* and *B*.

$$E_{\text{total}} = E_{\text{el}} + \sum_{B>A} \sum_{A} [C_A C_B (s_A s_A | s_B s_B) + f_{AB}]$$
(8)

Unlike the AM1 method, the PM3 method treats the onecenter, two-electron integration integrals (zz|yy) and (zy|zy) as fitting parameters. Also, the procedure that is used to optimize the atomic parameters differs significantly from the procedure described above [11].

#### 3.2. Molecular geometry optimization

The molecular dynamics simulations allow to optimize the molecular geometry structure corresponding to the minimum of the total energy as a criterion of self-consistent iteration convergence, for the molecule geometry optimization and electronic structure calculation we have chosen the convergent total energy criterion to be equal of about 0.014 eV which corresponds to the model approach. Addition information concerning the origin of absorption bands can be obtained by considering the electrostatic potential. Fig. 3 shows the total electrostatic potential for molecules derivatives calculated within AM1-procedure [12].

The substitution of the backside group changes drastically electrostatic distribution within the molecular chain. So it may be manifested also in the behavior of the optical spectra.

In general the band gap of the molecule **1–4** is the orbital energy difference between the highest occupied—an orbital that contains at least one electron molecular orbital— (HOMO) and the lowest unoccupied—an orbital that contains at least one open space for an electron—molecular orbital (LUMO) when the repeated unit number is infinite.

These orbitals are called the frontier orbitals, and determine the way the molecule interacts with other species. The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that has room to accept electrons [13–15]. Using the semiempirical all-valence semi-empirical AM1 and PM3 methods



Fig. 3. Total electrostatic potential for molecules derivatives calculated within AM1-procedure for styryloquinolines 1, 2, 3, 4. Balls: ●, carbon; ●, hydrogen; ●, nitrogen; ●, chlorine.

Table 1		
Energy values of HOMO	and LUMO fo	r stvrvloquinolines

Methods		Molecule 1			Molecule 2 M		Molecule	Molecule 3			Molecule 4		
		HOMO (eV)	LUMO (eV)	$ \Delta E $	HOMO (eV)	LUMO (eV)	$ \Delta E $	HOMO (eV)	LUMO (eV)	$ \Delta E $	HOMO (eV)	LUMO (eV)	$ \Delta E $
AM1	0	-7.60	-1.41	6.19	-8.15	-1.28	6.87	-8.22	-1.40	6.82	-10.99	-4.89	6.90
	20	-12.74	3.41	16.15	-20.44	3.60	16.84	-12.59	3.48	16.07	-11.72	0.58	12.30
	40	-16.21	4.38	20.59	-25.08	4.37	20.71	-15.63	4.34	19.97	-17.04	2.88	19.29
	60	-26.55	5.46	32.01	-35.85	5.11	29.74	-23.84	5.12	28.96	-25.21	4.85	30.06
PM3	0	-9.22	-2.55	6.67	-8.17	-1.49	6.68	-8.02	-1.56	6.46	-12.03	-5.05	6.98
	20	-12.90	2.72	15.62	-12.65	3.01	15.66	-12.76	2.96	15.72	-15.54	0.14	15.68
	40	-16.33	3.91	20.24	-18.04	3.93	21.97	-15.59	3.81	19.40	-17.19	2.91	20.01
	60	-24.11	5.37	29.48	-21.20	4.93	26.14	-21.79	4.95	26.74	-29.20	4.41	33.61

The HOMO and LUMO energies are originated from the atomic orbital energies of the carbazol group and agreed well with experimental data (5.1 eV).

has been calculated of theoretical values HOMO and LUMO for molecule **1–4** (Table 1).

# 3.3. Experimental and theoretical absorption and photoluminescence spectra

The optical spectra were simulated by the two semiempirical methods—AM1 and PM3. The electronic transition spectra were calculated considering only the singly excited configuration interactions. Seven electrovolt limited the criteria regarding the excitation energies or orbital occupation criterion (3 occupied and 3 unoccupied orbitals). The UV absorption spectra were recorded in tetrahydrofuran solution using Shimadzu UV–vis 2101 scanning spectrophotometer in range 200–800 nm. Solution measurements were performed using standard 1 cm path length quartz crucible for absorption spectrometry.

The calculations were done for two type of isomers (*cis*and *trans*-). However, experimentally we are able to measure only *trans*-compounds of the investigated molecule. From the Fig. 4, one can clearly see that the AM1 method gives better agreement compared to the PM3 ones. At the same time it is a bit surprisingly that *cis*- and *trans*-isomerisation should not play substantial role in the spectra simulated. Several broadening of the UV-absorption spectra is caused by electron-vibration interactions of the pure molecular electronic transitions.

The intensity of optical absorption is determined by the following expression:

$$A_{x,y,z} \approx \omega \sum_{j=1}^{n} \sum_{i=x,y,z} |\mu_j^{(x,y,z)}|^2 \exp\left(-\left(\frac{E-E_j}{H}\right)^2\right)$$
(9)

Table 2 The theoretical maximum peaks absorption of styryloquinolines 1–4 where *j* is the number of transition from ground state;  $E_j = h\omega j$ the transition energy;  $\mu_j^{(x,y,z)}$  the transition dipole component hale Bern obtained directly within AM1 and PM3 procedure; *H* the damping (value of about 0.12 eV, what gives the best agreement in contour shape of calculated optical absorption spectra compared to experimental data).

Measured absorption spectra of styryloquinolines and the calculated absorption spectra (H=0.12 eV) are presented in the Fig. 4. One can see that experimental absorption spectra of styryloquinolines and calculated within the AM1 and PM3 methods are rather similar. They can be characterized generally by two relatively strong absorption bands. We observed the theoretical peaks absorption (see Table 2).

The corresponding experimental spectra have in all the cases an absorption threshold at about 241 nm which appears to be in fairly good agreement with quantum chemical simulations, namely for the spectra calculated by AM1 method. It is also amazing that spectral positions of the most strongest broad absorption bands at about 241 nm in the measured spectra well coincide with the calculated spectra. Both quanta–chemical methods give here sufficiently good agreement, but AM1 method is better than PM3

Measured photoluminescence spectra of styryloquinolines and the calculated spectra (H = 0.12 eV) are presented in the Fig. 5.

The intensity of photoluminescence spectra is determined by the following expression:

$$I_{\rm PL}(\omega) = \omega^4 \sum_{j=1}^n \frac{\sum_{i=x,y,z} (M_j^{(x,y,z)} - M_0^{(x,y,z)})^2}{(\omega - \omega_j)^2 + (H/2)^2}$$
(10)

where *j* is the number of transitions form ground state *g* to excited state;  $\omega_i$  the corresponding transition frequencies

Theoretical peak	Molecule	e 1, $\lambda_{max}$ (nm)	Molecule	$2, \lambda_{\max} (nm)$	Molecule 3, $\lambda_{max}$ (nm)		Molecule 4, $\lambda_{max}$ (nm)	
	AM1 <sup>a</sup>	PM3 <sup>a</sup>	AM1 <sup>a</sup>	PM3 <sup>a</sup>	AM1 <sup>a</sup>	PM3 <sup>a</sup>	AM1 <sup>a</sup>	PM3 <sup>a</sup>
cis	241	258, 290	244	255	241	278	244	252
trans	242	260, 286	245	250	241	275	245	260

<sup>a</sup> Method.

 $(Ej/h); M_j^{(x,y,z)}, M_0^{(x,y,z)}$  the excited and reference state dipole component, respectively and *H* is the damping.

We found that experimental and theoretical photoluminescence spectra in fairly good agreement. The spectrum of photoluminescence (PL) was observed in the range 400-700 nm.

From Fig. 5 one can see that the general view of the theoretical photoluminescence spectra may be described



Fig. 4. Measured absorption spectra of the styryloquinolines (the experimental absorption spectra of the molecules dissolved in the tetrahydrofuran) and calculated spectra within the semi-empirical quantum chemical PM3 and AM1 models. Inset shows the chemical structure of styryloquinolines obtained within the geometrical optimization procedure has been carried out by (MM+) mode. The theoretically absorption spectra calculated of the investigated molecules in the vacuum.



Fig. 4. (Continued).

The	theoretical	maximum	peaks	potoluminescence	of sty	rvloa	uinolines 1	-4
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Theoretical peak	Molecule	$1 \lambda_{max} (nm)$	Molecule	blecule 2 $\lambda_{max}$ (nm) Molecule 3 $\lambda_{max}$ (nm)		Molecule 4 $\lambda_{max}$ (nm)		
	AM1 <sup>a</sup>	PM3 <sup>a</sup>	AM1 <sup>a</sup>	PM3 <sup>a</sup>	AM1 <sup>a</sup>	PM3 <sup>a</sup>	AM1 <sup>a</sup>	PM3 <sup>a</sup>
cis	475	525	470	525	475	490	475	530
trans	500	525	460	531	477	500, 525	480	525

<sup>a</sup> Method.

Table 3



Fig. 5. Measured photoluminescence spectra of the styrylochinolines (the experimental absorption spectra of the molecules dissolved in the chloroform) and calculated spectra within the semi-empirical quantum chemical PM3 and AM1 models. The theoretically photoluminescence spectra calculated of the investigated molecules in the vacuum.



Fig. 5. (Continued).

by several maxima and are relatively similar. In particularly we can see that the experimental photoluminescence peaks obtains for molecule at about 475 nm. The same figure represented the theoretical photoluminescence peaks. We observed the theoretical peaks photoluminescence (see Table 3).

The absorption and photoluminescence spectra give important information concerning the quantum chemical

states and may serve as a powerful tool for understanding the nature of the observed absorption and related luminescence. At the same time, these calculations (experimental and theoretical) may give an advice for directed changes of the specific molecular structure.

#### 4. Conclusion

A method of synthesis several 6-styrylo1-1*H*-pyrazolo [3,4-b]quinolines was proposed. Particularly, 6-styryl-1,3-diphenyl-1*H*-pyrazolo[3,4-b]quinolines were prepared by Wadsworth–Emmons reaction. One of advantageous of these materials is stability of their optical spectra versus the possible *cis*- and *trans*-transformation.

In this paper we presented experimental and theoretical study of the optical absorption and photoluminescence excitation spectra for styryloquinolines. We have calculated electrostatic potential and value of the HOMO–LUMO energy gap of these molecules, too.

A satisfaction agreement between the theoretical calculated and experimentally measured spectra was observed. One of advantageous of these materials is stability of their optical spectra versus the possible *cis- trans*-transformation.

Theoretical and experimental studies of optical absorption and photoluminescence excitation spectra for styryloquinolines were done. They show that the AM1 semi-empirical method gives better results compared to other approaches. We have found that the solvents do not play a role in the behavior of the spectra. The backside-substituted groups do not influence substantially the observed optical spectra.

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