Time-dependent DFT simulation of UV- spectra and molecular structure of several bis-pyrazolopyridines derivatives

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Quantum chemical simulations of UV-absorption spectra in substituted bis-pyrazolopyridines were done. As a theoretical tool we have applied time dependent density functional theory (TDDFT) method with Vosko – Wilk – Nusair parameterisation. Comparison of the theoretically calculated UV-absorption spectra with experimental data was performed. Crucial role of π-conjugated bonds within the backside phenyl rings is demonstrated. Physical insight of the several observed discrepancies between calculations and experimental data is discussed. Comparison of the TDDFT and several semi-empirical approaches is given. Crucial role of aromatic bonds is demonstrated.

1. Introduction

Recently one can observe an increasing interest to non-linear optics (NLO) organic and polymeric systems, because of their potential applications in optoelectronic and optical devices [1]. Especially are investigated materials possessing interesting charge transport features which may be used as materials for electroluminescent devices [2, 3]. The number of organic electron-transporting materials is very limited. Pyrazolo[3,4-b]-quinoline and its derivatives [3] show interesting charge transport properties in addition to their fluorescent properties in blue spectral range [4]. Bis-pyrazolopyridine (PAP) derivatives are similar to pyrazolo[3,4-b]quinoline by molecular structure. Electron transport properties of these materials were reported in Ref. 5. Some of them, for example 4-(4'-N,N-dimethylaminophenyl)-3,5-dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b;4',3'-e]-pyridine (PAP5) are representative chromophore with electron donor – acceptor subunits and was explored by fluorescence spectroscopy [6] and it was found strongly solvent dependent [7]. Moreover, organic molecules of conjugated π-electron system terminated with donor and acceptor groups show large optical hyperpolarizabilities [8, 9]. Amorphous polymers involving incorporated molecules with large first hyperpolarizabilities show interesting NLO properties [10], particularly second harmonic generation (SHG) [11, 12]. To find appropriate guest – host material one should find a chromophore possessing collinear state dipole moment with polymer in order to achieve increasing transition dipole moment [13].

The search of the organic materials with improved charge transfer (CT) properties requires precise quantum chemical calculations of space charge density distribution, state and transition dipole moments, HOMO and LUMO states. The absorption in the range of UV spectrum was taken as a main criterion for verification of performed quantum chemical calculations. The density functional theory (DFT) approach introduced by Kohn and Sham seems to be a powerful one – electron quantum chemical method. Recently it was shown that time – dependent density functional theory (TDDFT) method reproduces very accurately optical susceptibilities for a wide range of organic systems [14, 15].

Up today all the calculations of bis-pyrazolopyridines derivatives using semi-empirical methods were performed [5]. Comparison of experimental and theoretical spectra gives possibility to clarify role of solvatochromic effects as well as electron – vibration broadening. Generally absorption spectra play key role in understanding of the electro – optical properties.

In the present work, computer simulations of the PAP derivatives were performed using TDDFT method and it was further compared with experimental absorption spectra using chloroform as solvent. The chemical structures of PAP molecules are presented in Fig. 1

In Sec. 2 experimental methods applied are described. Sec. 3 is devoted to chosen theoretical approach. Sec. 4 compares evaluated spectra with the experimental ones. Sec. 4 compares evaluated spectra with the experimental ones and analyse the discrepancies observed.

2. Experimental part

The specification of all the investigated molecules is given in Fig. 1. Synthetic procedures of PAP derivatives were presented in early work [20]. All other chemicals and spectrally pure or Analar grade solvents were obtained from BDH, Aldrich or GEC products. UV absorption was measured using a Hewlett Packard 8452A diode array spectrophotometer with spectral resolution about 1 nm/mm. Solution measurements were performed using a standard 1 cm path length quartz crucible. The doped polymer films were also prepared either by solution casting or spin coating onto optical glass microscope slides or quartz slides. The film thicknesses were about 0.5-2 μm and were monitored using a calibrated Talysurf profilometer.

3. Theoretical simulations

The UV-absorption spectra were calculated using method presented in work [51]. The integration is performed over real $\vec{r}$ space. The intensity of absorption is proportional to transition dipole moment $\vec{\mu}_{jk}$ from ground *j*-th to *k*-th excited level and can be evaluated by formula:

$$I_{jk} \approx \omega_{jk} \frac{(\mu_{jk})^2}{\hbar\omega_{jk} - \hbar\omega \pm i\Gamma_{jk}} \tag{1}$$

where $\hbar\omega_{jk}$ is difference of energies between ground *j* and excited *k* and $\hbar\omega$ is the input running radiation energy. Γ_{jk} - line broadening is inversely proportional to the lifetime of $|k\rangle$ state and determines by the electron – vibration broadening.

The geometry of molecules was optimised using DFT theory in a frame of formalism included in Amsterdam Density Functional (ADF) package [22-24]. According to the size of samples, all calculations were performed using a basis functions known as double zeta Slater-type orbitals (DZ) [25-27] and local density approximation (LDA) in which the exchange-correlation V_{xc} potential is a local functional of electron density. Core electrons as well as atopmic positions were kept frozen within Born – Oppenheimer approach. The Broyden – Fletcher – Goldfarb - Shanno (BFGS) method [27] was chosen to update Hessian matrix. The gradient convergence criterion was chosen to be 0.001 au/Å which corresponds to 100 iterations.

In this paper, the excited states of PAP derivatives are studied using the TDDFT approach [28-32]. It is a promising method for calculation properties for many-electron systems [33]. Contrary to the semi-empirical approaches by which these systems have been studied before [5], TDDFT is based on a first principles theory, which only recently has enabled the study of excitation energies, oscillator strengths and polarizabilities of systems possessing such size.

TDDFT approach usually provides a good accuracy in calculation of excitations energies, which exceeds those from configuration interaction (CI) method and is often comparable in accuracy to the most advanced *ab initio* approaches [34-36]. All quantum chemical calculations reported in the present work have been performed using the ADF-RESPONSE module [37], which is an extension of the ADF package. It was applied local density approximation (LDA) potential with Vosko – Wilk – Nusair parameterisation [38]. All the calculations were performed using a triple zeta Slater-type basis [39, 40] augmented with two polarization functions. The used basis set was not extended with diffuse functions according to the number of atoms in molecule. The self-consistent field (SCF) procedure was determined by convergence criterions: maximum number of iterations 100, the energy convergence criterion 10^{-8} Hartrees. The excitation energies were calculated using iterative Davidson method with a tolerance of energy 10^{-12} Hartrees. Orthonormality of the trial vector in Davidson algorithm was 10^{-14}. The algorithm can be converged during 200 iterations.

4. Results and discussions

The crucial bending angles studied during calculations are defined in Figure 1 and Figure 2. The principal parameters of the optimised molecular structures resulted from the calculation are presented in Table I. The presented total energies are calculated by DFT method and fro comparison by semi-empirical methods: namely AM1 and PM3. The lowest total energy (E_{tot}) of the considered molecules gives the AM1 method but for all the samples the tendency for all used methods is preserved. The most thermodynamically stable (possessing less E_{tot}) are molecules PAP3 and PAP5. The phenyl (Ph) groups substituted in position R_2 and R_3 drastically diminishe the E_{tot} of the considered structures. The phenyl rings in the substituted bis-pyrazolopyridines can be rotated around N – C bonds. The substitution of the PAP derivatives by Ph group in position R_2 and R_3 changes the geometry of bond R_1. The group substituted in position R_1 is more twisted for all molecules with Ph groups in position R_2 and R_3. For the PAP3 and PAP4 the torsion angle ω is almost 90^o. The angles α and β change themselves simultaneously for all the considered molecules. However, as reported in reference 41, where the semi–empirical methods were used, the minimum energy for the molecule PAP2 was achieved when the angles α, β were equal to 40^o and the ω angle was varied from 70^o up to 120^o. This discrepancy may reflect non-complete basis set within a ground state. In reference 41, the ground state geometries of the full chemical structures were optimized using Austin model (AM1) [42]. The structural optimisation of the PAP3 molecule by DFT method, used in this work, gives results similar to that obtained in the Ref. 41. In both cases the substituted methoxybenzene group is almost perpendicular to the heterocycle. The bending angle γ for the substituted methoxy group in PAP3 is equal to 117^o. The bending angle γ of the dimethylamino group in PAP5 is higher than for methoxy one in PAP3 and is equal to 120^o. The improper dihedral angle for the 3-phenyl group and N in dimethylamino group is 180^o. This is in agreement to the results obtained in Ref. [41] by semi-empirical methods. The Figure 3 presents the experimentally measured UV – absorption spectra for all the considered bis-pyrazolopyridines derivatives. One can see that the shape of spectra is very similar for molecules PAP2 – PAP5. The important difference is only for molecule PAP1 which does not posses aromatic group as substituent.. One can see the same number of peaks but their intensities are changed. The absorption maxima for PAP1 molecule are shifted in the blue region compared with other ones. It is related to the substitute methyl groups in positions 2 and 3. The peaks for molecules PAP2 – PAP5 denoted as A are doubly split but for molecule PAP5 the peaks A' and A'' are broad and the splitting is not so clear as for other molecules. The difference between the intensity of the A'/A'' ration is highest for the PAP5 molecule. Probably the split of the peak A is associated with position of phenyl group in the places 2 and 3. Positions of all the considered peaks are collected in the Table II. The ratio of the intensity for the peaks B/C is similar for all the molecules except PAP1. The difference between A'/B and A''/B is the same for all the considered molecules and has the lower value when in position 1 is the phenyl group.

In the Figure 4 spectra of PAP1 and PAP4 molecules calculated by TDDFT method are presented. Theoretically obtained UV – absorption spectra calculated by TDDFT method for PAP2, PAP3 and PAP5 molecules have similar shape. For all the considered samples, theoretical spectra are red-shifted compared to the experimental ones (see the Table II) which is typical for the DFT approach. More substantial difference is observed for the peak A for molecules PAP2 – PAP5. In the experimental spectra the A peak is doubly split in comparison to the theoretical calculations. It might be caused by electron-vibration broadening, which is not included into the actual pure electronic theoretical calculations. The controversial problem exists for PAP1 molecule, because the TDDFT method does not reproduce sufficiently its UV absorption spectrum. Particularly, the ratio of the A to B maximum's intensity for the theoretical and experimental spectra is inversed. The transition dipole moments are affected by the geometry of the molecule and the rotation angle of the phenyl groups. In our calculations the solvatochromic spectral shift was not taken into account. In the work of Piorun et al. [43] UV-absorption spectra of the bis-pyrazolopyridine derivatives in different solvents were investigated and give results very similar to our experimentally measured ones. The maximum of UV-absorption for the PAP5 molecules in the $HClO_4$ was placed at λ=256 nm [43]. Surprisingly it is exactly the same value as in our work for PAP5 in chloroform. This means that the PAP derivatives are almost non-sensitive to the solvatochromic effect. The figures 5 and 6 present theoretical UV – absorption spectra computed by semi-empirical AM1 and PM3 methods. For convenience we present only three bis-pyrazolopyridine derivatives because the UV – absorption spectra for PAP3 and PAP4 molecules are very similar to the calculated for PAP2 and PAP5. The geometry of molecules was the same as described above.

One can see that both the semi-empirical methods give spectra blue-shifted compared to the TDFT calculated ones. It is connected with the HOMO-LUMO energy splitting presented in Table III. The meta-stable states obtained by TDFT method are energetically less favourable than these obtained by semi-empirical methods. The spectral positions of UV – absorption maxima calculated by semi-empirical methods are closer to the experimentally observed values than these calculated by the TDFT ones (see Table II). The best approximation for peaks denoted as B and C gives the PM3 method but to reproduce the position of peaks A better is the AM1 method. It is associated to the parameters used in both methods. The peak A originates from pyrazolopyridine skeleton group interacting with substitutes. For the both semi-empirical methods (AM1 and PM3) the spectra for PAP1 molecule are blue-shifted compared to other considered samples and correlate well with experimental results. So one can say that theoretical calculations of the UV-absorption spectra can reproduce the spectral position of absorption maxima, but TDFT method gives better shape of spectra, which are-red shifted.

For convenience in the Table III are presented the calculated dipole moments calculated by different methods. The highest value of dipole moment for all the molecules except PAP1 gives the DFT method. One can see that the methoxy and dimetyloamino groups enhance the static dipole moments of the molecule. The molecules PAP3 and PAP5 might be promising compounds for nonlinear-optical applications. These investigations are in progress. From the Table II it is seen also that the values of gaps between HOMO and LUMO are very small. It is well-known that the occupied and unoccupied eigenvalues are too close together in the LDA approach [44] causing crucial frequency dependence. To obtain the correct static third-order hyperpolarizability, which is proportional to the HOMO-LUMO energy difference, Zhong and co-workers [45] used GW model [46,48] to shift unoccupied energies by a constant rescaling value. In our case, the spectral shift of the UV-absorption spectra for the PAP2, PAP3, PAP4 and PAP5 is almost the same and is equal to 100 nm and we can apply blue-shifting rescaling factor.

The LDA potential shows the erroneous behaviour in the outer region and gives the accurate V_{xc} potential near the nucleus. One can suppose that the molecular geometry optimization using this potential is correct and the shift of the UV- spectra is not related to the uncorrected optimized molecular geometry. The LDA approximation can only take into account the local part of the electron–electron correlations, which do not deal with long-range correlation at sufficient accuracy [48]. Generally the generalized approximation (GGA) method gives more accurate results of the excited states calculations but not for all the molecules. Parac and Grimme [49] have studied the lowest excitation energies by BP86 and B3LYP potential for polycyclic aromatic hydrocarbon and they have obtained the error for the excitation energy up to 0.75 eV. The TDDFT method is very sensitive to the number of π-conjugated carbon bonds. The excitation energies calculated by the DFT theory are relatively insensitive to the choice of basis set. The difference across double and triple zeta basis set never exceeds 0.13 eV [50].

Conclusions

The performed molecular dynamics simulations of pyrazoliones have shown that for all the considered samples, the heterocycle is planar and the substituted phenyl rings in position 2 and 3 are slightly twisted. The 3-phenyl group in PAP1 (without aromatic substituents) is twisted neither the absence of the phenyl groups in position 2 and 3. The steric effect of 3-phenyl group is due to presence of the neighbouring methyl groups. The methoxy and dimethylamino groups more twist the 3-phenyl group in position 1 than Ph groups in these positions. There is no interaction between 3-phenyl group in position 1 and the 2- and 3-phenyl groups rotation.

The LDA method can reproduce fairly good the UV absorption spectra of the PAP derivatives with taking into account blue-shifted rescaling factor. The rescaling factor is not caused by the solvatochromic effect. The slight difference between UV absorption spectra of the PAP2-PAP5 molecules is due to the auto-chromic effect of the dimethylamino group, thus enlargement the π-electronic system. The DFT method including the electron system can not reproduce the doubling of the maximal peak absorption. The molecules PAP3 and PAP5 might be promising materials for the nonlinear optical applications. One can say that theoretical calculations of the UV-absorption spectra can reproduce the spectral position of absorption maxima, but TDDFT method gives better shape of spectra, which are-red shifted. The TDDFT method is very sensitive to the number of π-conjugated carbon bonds. The excitation energies calculated by the DFT theory are relatively insensitive to the choice of basis set. The difference across double and triple zeta basis set never exceeds 0.13 eV

References

1. Polymers for Lightwave and Integrated Optics: technology and Applications; L.A. Hornak, Ed., Marcel Dekker: New York, NY, **1992**.
2. C.W Tang, S.A. Van Slyke, *Appl. Phys. Lett*. 51 (1987) 913
3. A.R. Tameev, Z.He, G.H. Milbum, A.A. Kozlov, A.V. Vannikov, A. Danel, P. Tomasik, *Appl. Phys. Lett.* 77 (2000) 322
4. Z. He, G.H.W. Milburn, K.J. Baldwin, D.A. Smith, A. Danel, P. Tomasik, *J. Lumin.* 86 (2000) 1
5. A.R. Tameev, Z.He, G.H.W. Milburn, A.A. Kozlov, V. Vannikov, A. Puchala, D. Rasala, *Appl. Phys. Lett.* 81 (2002) 969 .

6. K.Rotkiewicz, K. Rechthaler, A. Puchala, D. Rasala, S. Styrch, G. Kohler, J. *Photochem. Photobiol. A: Chem* 98 (1996) 15
7. H. Miyasaka, A. Itaya, K. Rodkiewicz, K. Rechthaler, *Chem. Phys. Lett.* 307 (1999) 121
8. A. Dulcic, C. Sauteret, *J. Chem. Phys.* 69 (1978) 3453.
9. J.Y. Lee, K.S. Kim, B.J. Mhin, *J. Chem. Phys.* 115 (2001) 9484.
10. C.Bosshard, K. Sutter, P. Pretre, J. Hullinger, M. Florsheimer, P. Kaatz, P. Gunter, Organic Non-linear Optical Materials, Gordon and Breach, Basel, 1995
11. Y.S. Cho, J.S. Lee, G. Cho, T. Wada, H. Sasabe, *Polymer* 42 (2001) 9379.
12. W.J. Kuo, G.H. Hsiue, R.J. Jeng, *J. Mater. Chem.* 12 (2002) 868.
13. I.V. Kityk, B. Sahraoui, I. Ledoux-Rak, M. Salle, T. Kazuo, A. Gorgues, Mater. Sci. Eng. 87 B (2001) 148
14. M.E. Casida, in D.P. Chong (Ed.) Recent Advances in Density Functional Methods, vol. 1, World Scientific, Singapore, (1995)
15. F. Furche, R. Ahlricks, A. Sobanski, F Vogtle, C. Wacksman, E. Weber, S. Grimme, J. Ame. Chem. Soc. 122 (2000) 1717
16. A.D.Becke, Phys. Rev. A 38 (1988) 3098
17. J.P. Perdew, Phys. Rev. B 33 (1986) 8822
18. A.D. Becke, J. Chem. Phys. 98 (1993) 5648
19. P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623
20. Z. He, A. Donel, G.H.W. Milburn, A. Puchala, P. Tomasik, D. Rasala, J. Mater. Chem. 7 (1997) 2323
21. Atomic, molecular &optical physics, Gordon W. F. Drake, Woodbury, New York, 1996
22. E.J. Berends, D.E. Ellis, P. Ros, Chem. Phys. 2 (1973) 41
23. G. te Velde, E.J. Berends, J. Comp. Phys. 99 (1992) 84

24. C. Forseca Guerra, O. Visser, J.G. Snijders, G. te Velde, E.J. Berends, Parallelisation of the Amsterdam Density Functional Program. In Methods and Techniques for Computational Chemistry; E. Clementi, G. Corongiu, EDS.; STEF: Cagliari, 1995; pp 305 – 395
25. J.G. Snijders, P. Vernooijs, E.J. Baerends, At. Data. Nucl. Data. Tabl. 26 (1981) 483
26. A. Schafer, H. Horn and R. Ahlrichs, J. Chem. Phys. 97 (1992) 2571.
27. T.H. Dunning Jr., J. Chem. Phys., 53 (1970) 2823.
28. E. Runge and E. K. U. Gross, Phys. Rev. Lett. **5**2 (1984) 997
29. E. K. U. Gross and W. Kohn, Adv. Quantum Chem. **2**1 (1990) 255
30. R. van Leeuwen, Int. J. Mod. Phys. B **1**5 (2001) 1969
31. S.J.A. van Gisbergen, *Molecular Response Property Calculations using Time Dependent Density Functional Theor*y, in *Chemistr*y. 1998, Vrije Universiteit: Amsterdam. p. 190.
32. E.K.U. Gross, J.F. Dobson, and Petersilka, in *Density Functional Theor*y, R.F. Nalewajski, Editor. 1996, Springer: Heidelberg.
33. M. van Faassen, P. L. de Boeij, R. van Leeuwen, J. A. Berger, and J. G. Snijders, Phys. Rev. Lett. 88 (2002) 186401
34. G. Ricciardi, A. Rosa, S.J.A. van Gisbergen, E.J. Baerends, J. Phys. Chem. 104 (2000) 635
35. S.J.A. van Gisbergen, J.A. Groeneveld, A.Rosa, J.G. Snijders, E.J. Berends, J. Phys. Chem. A 103 (1998) 6835
36. A. Rosa, E.J. Berends, S.J.A. van GisbergenE. Van Lenthe, J.A. Groeneveld, J.G. Snijders, J. Am. Chem. Soc. 121 (1999) 10356
37. S.J.A. van Gisbergen, J.G. Snijders, E.J. Berends, Comput. Phys. 118 (1999) 119
38. S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200

39. K.G. Dyall Journal: Theor. Chem. Acc. 108 (2002) 335; erratum Theor. Chem. Acc. 109 (2003) 284.
40. J. Dunning, J. Chem. Phys. **55**, 716 (1971).
41. A.B.J. Parusel, R. Schamschule, D. Piorun, K. Rechthaler, A. Puchala, D. Rasala, K. Rotkiewicz, G. Kohler, J. Mol. Struct. 419 (1997) 63
42. H.Zhong, Z.H. Levine, J.W. Wilkins, Phys. Rev. A 43 (1991) 4629
43. D. Piorun, A.B.J. Parusel, K. Rechthaler, K. Rotkiewicz, G. Kohler, J. Photochem and Photobiol. A 129 (1999) 33
44. L. Reining, V. Olevano, A. Rubio, G. Onida, Phys. Rev. Lett. 88 (2002) 66404
45. H.Zhong, Z.H. Levine, J.W. Wilkins, Phys. Rev. A 43 (1991) 4629
46. L. Hedin, S. Lundqvist, Phys. Rev. A 139 (1965) 796
47. L. Hedin, S. Lundqvist, Solid State Phys. 23 (1969) 1
48. E.K.U. Gross, J.F. Dobson, M. Petersilka, in: R.F. Nalewajski (Ed.), Density Functional Theory II, Springer Series in Topics in Current Chemistry, Band 181, Springer, Heidelberg, 1996
49. M. Parac, S. Grimme, Chem. Phys. 292 (2003) 11
50. C. Jamorski, M.E. Casida, D.R. Salahub, J. Chem. Phys. 104 (1996) 5134
51. M.Makowska-Janusik, J.Sanetra, H.Palmer, D.Bogdal, E.Gondek, I.V.Kityk. Eur. Polymer Journal, **40** (2004), 799.

Table I. Principal molecular structure parameters of the considered bis-pyrazolopyridines derivatives

Molecule	Torsion angles			γ [^{o}]	Total energy [kJ/mol]		
	α [^{o}]	β [^{o}]	ω [^{o}]		DFT	AM1	PM3
PAP1	_____	_____	72	_____	-301949.33	-331852.50	-297543.75
PAP2	24	24	80	_____	-428502.82	-460477.50	-417375.00
PAP3	25	25	85	117	-462520.79	-506388.75	-460346.25
PAP4	28	28	80	_____	-431598.41	-466777.50	-420367.50
PAP5	20	20	86	120	-472496.55	-511777.00	463601.25

Table II. Positions of the peaks’ maxima of UV-absorption spectra obtained experimentally and calculated by DFT and semi-empirical methods

	A [nm]					B [nm]				C [nm]			
	Exp.		Theoretically calculated			Exp.	Theoretically calculated			Exp.	Theoretically calculated		
	A’	A’’	DFT	AM1	PM3		DFT	AM1	PM3		DFT	AM1	PM3
PAP1	246		291	235	Doubly split 245, 255	325	330	255	280	365	423	327	369
PAP2	260	278	349	273	292	330	395	298	317	375	470	329	373
PAP3	260	278	345	277	294	330	380	297	316	375	462	331	374
PAP4	258	279	346	269	287	330	405	296	315	379	480	334	376
PAP5	263	269	350	267	286	330	395	293	310	378	456	331	371

Table III. The dipole moments (μ), the HOMO-LUMO energies and the difference between them (ΔE) calculated by DFT and semi-empirical methods

Molecule	DFT				AM1				PM3			
	μ [D]	HOMO [eV]	LUMO [eV]	ΔE [eV]	μ [D]	HOMO [eV]	LUMO [eV]	ΔE [eV]	μ [D]	HOMO [eV]	LUMO [eV]	ΔE [eV]
PAP1	1.27	-5.09	-2.55	2.54	1.36	-8.60	-0.69	7.91	1.11	-8.34	-1.00	7.34
PAP2	3.79	-5.25	-2.83	2.42	2.72	-8.42	-0.82	7.60	2.07	-8.21	-1.09	7.12
PAP3	5.03	-5.20	-2.75	2.45	3.36	-8.40	-0.79	7.61	2.70	-8.19	-1.05	7.14
PAP4	0.57	-5.38	-3.01	2.37	0.08	-8.55	-0.98	7.57	0.57	-8.34	-1.24	7.10
PAP5	7.25	-5.07	-2.62	2.45	5.16	-8.31	-0.66	7.65	4.57	-8.10	-0.92	7.18

Figure captures:

Figure 1. Chemical formula of the PAP derivatives and definition of the characteristic dihedral angles

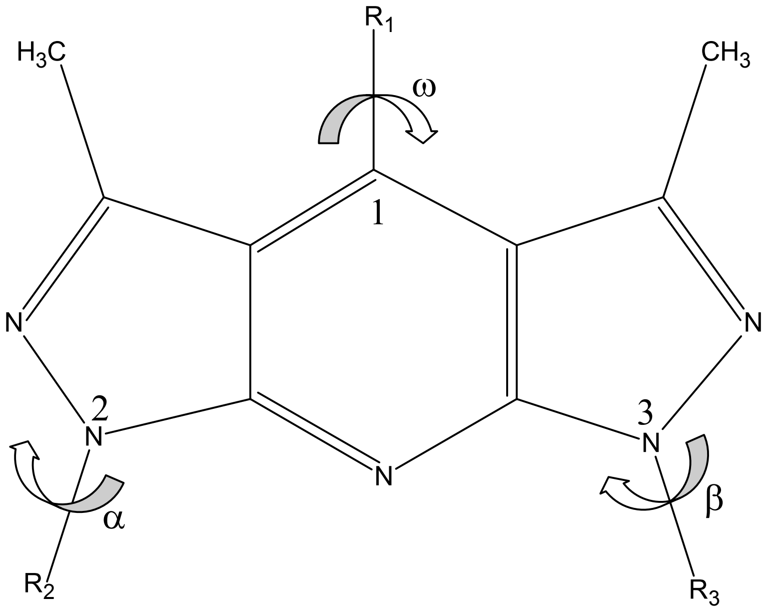
Fig. 2. Indication of the bending angle for PAP3 and PAP5 .

Fig. 3. Experimentally obtained UV – absorption spectra for all considered bis-pyrazolopyridines derivatives

Fig. 4. Theoretically obtained UV – absorption spectra for PAP1 molecule (solid line) and for PAP4 molecule (dashed line) calculated by TDDFT

Fig. 5. UV – absorption spectra computed by semi-empirical AM1 method for same bis-pyrazolopyridines derivatives

Fig. 6. UV – absorption spectra computed by semi-empirical PM3 method for same bis-pyrazolopyridines derivatives



	R_1	R_2	R_3
PAP1	Ph	CH_3	CH_3
PAP2	Ph	Ph	Ph
PAP3	Ph-O-CH_3	Ph	Ph
PAP4	Py	Ph	Ph
PAP5	Ph-N$(CH_3)_2$	Ph	Ph

Fig. 1.

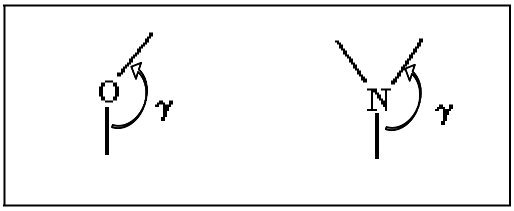


Fig. 2.

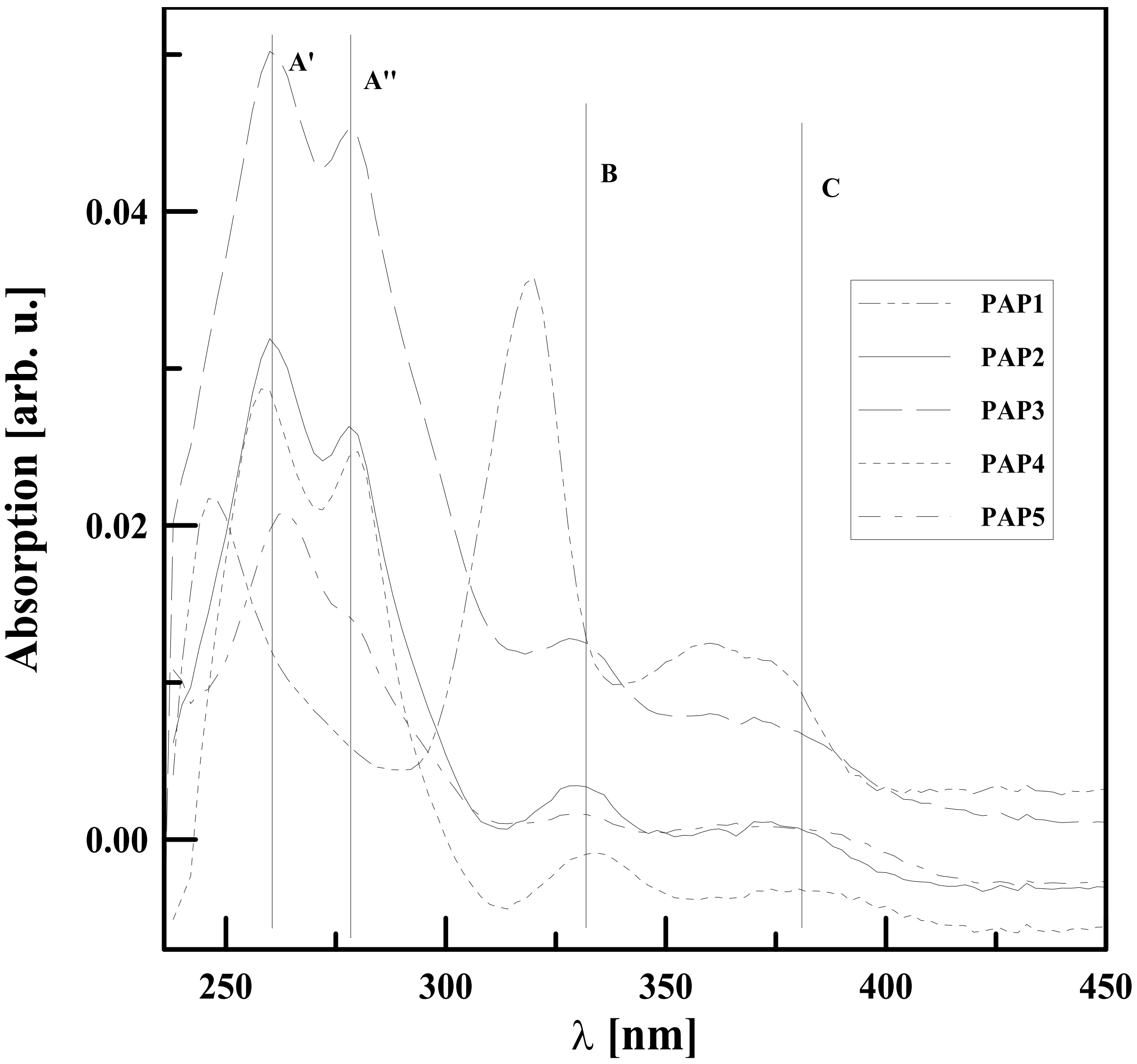

A'
A''
B
C
PAP1
PAP2
PAP3
PAP4
PAP5
0.04
0.02
0.00
Absorption [arb. u.]
250
300
350
400
450
λ [nm]

Fig. 3

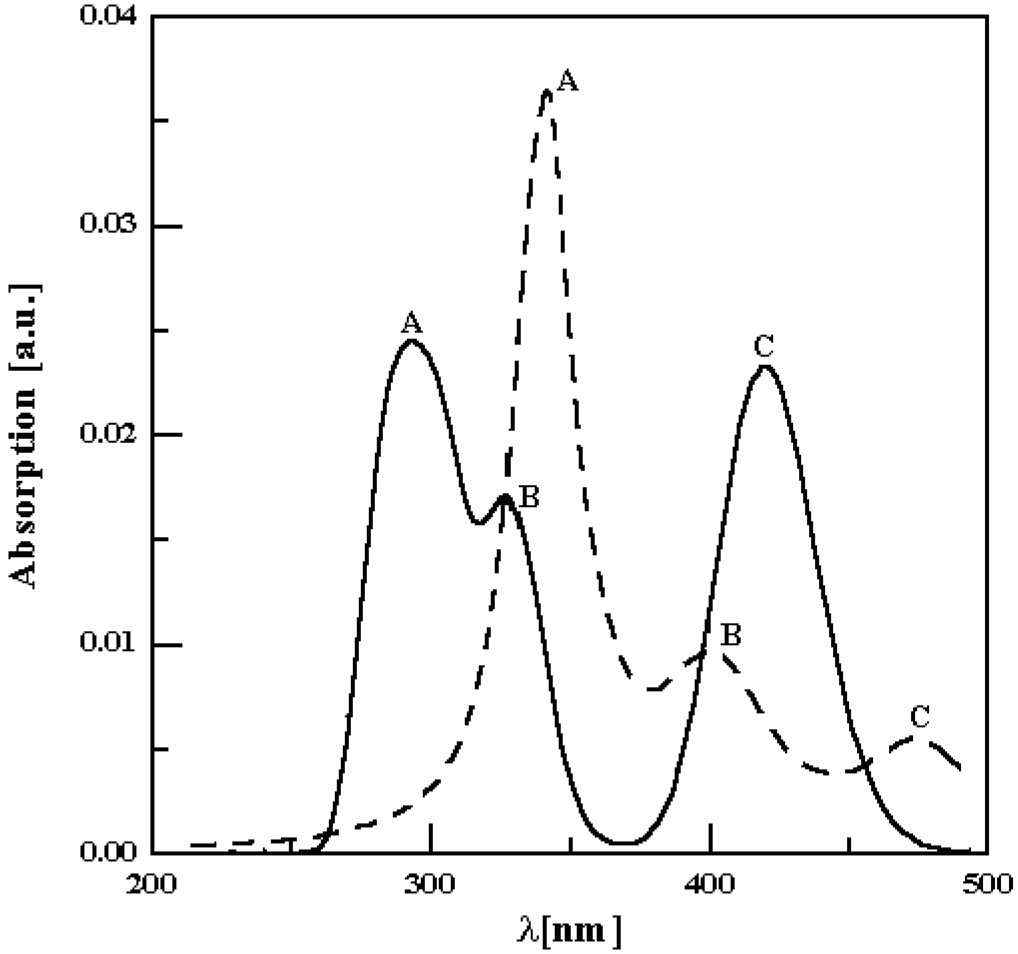


Fig. 4.

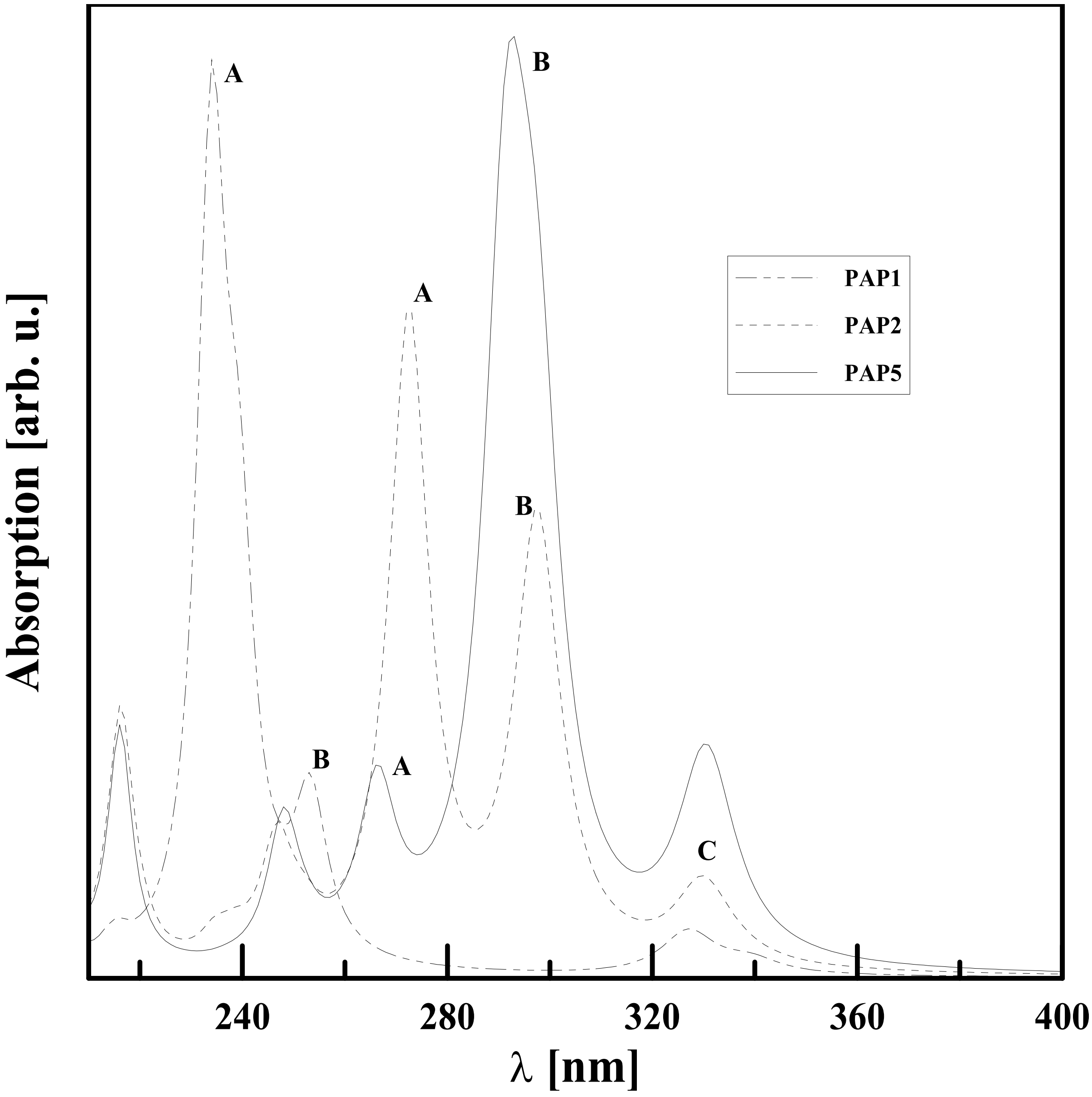

Absorption [arb. u.]
λ [nm]
240
280
320
360
400
A
B
A
B
B
A
C
PAP1
PAP2
PAP5

Fig. 5.

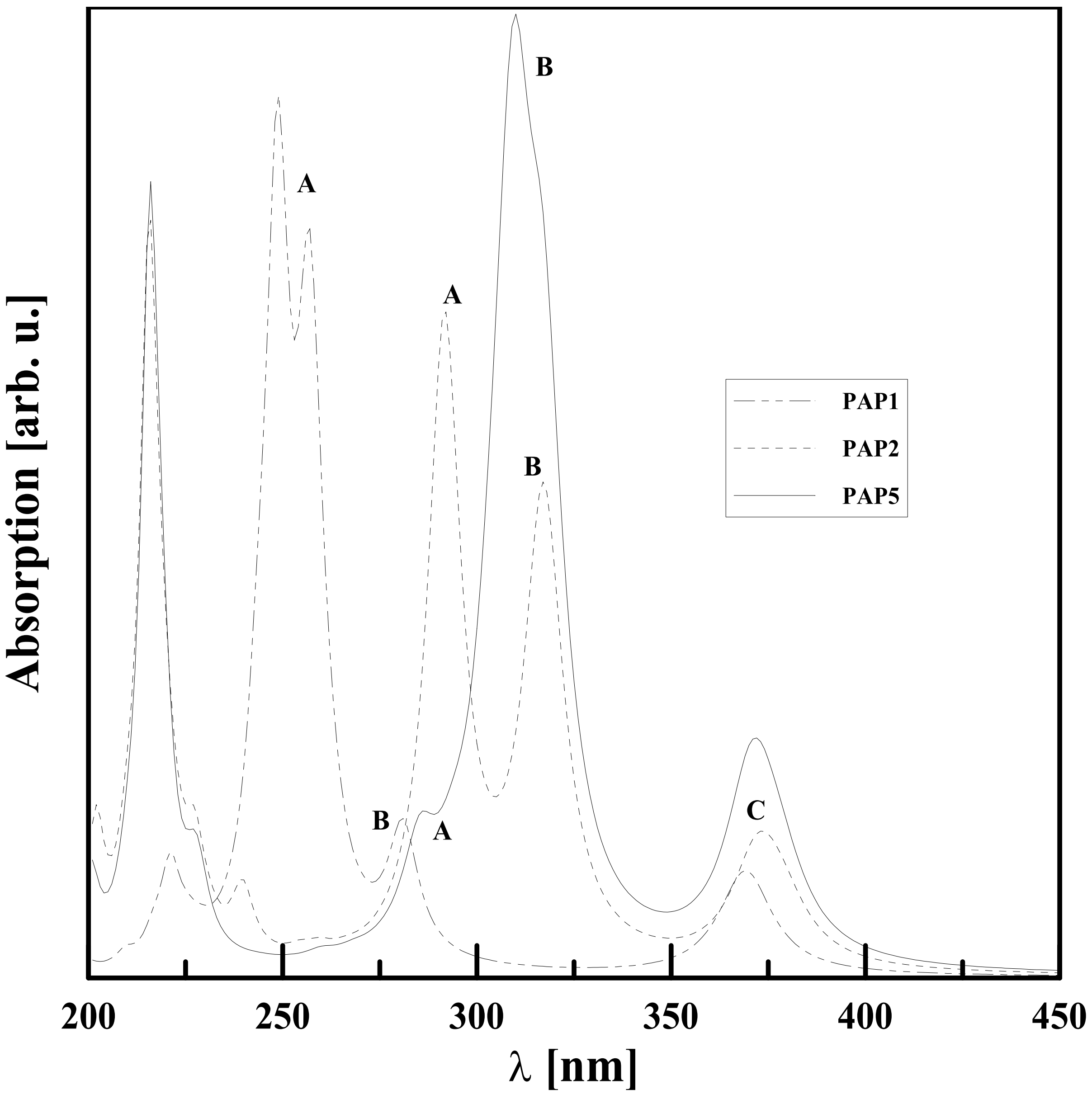

B
A
A
B
B
A
C
PAP1
PAP2
PAP5
Absorption [arb. u.]
200
250
300
350
400
450
λ [nm]

Fig. 6.