



Excited states of selected hydrazo-compounds on the example of 5-nitro-2-(2-phenylhydrazinyl)pyridine and its 3-, 4- or 6-methyl isomers

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ABSTRACT

Syntheses of 5-nitro-2-(2-phenylhydrazinyl)pyridine (5-nitro-2-phenylhydrazopyridine), 3-methyl-5-nitro-2-(2-phenylhydrazinyl)pyridine (3-methyl-5-nitro-2-phenylhydrazopyridine), 4-methyl-5-nitro-2-(2-phenylhydrazinyl)pyridine (4-methyl-5-nitro-2-phenylhydrazopyridine) and 6-methyl-5-nitro-2-(2-phenylhydrazinyl)pyridine (6-methyl-5-nitro-2-phenylhydrazopyridine) have been described. Electronic absorption and emission spectra of the compounds in the solid state and in various solvents have been measured at room temperature and discussed in terms of DFT quantum chemical calculations. The molecular structures and energy sequences of the singlet and triplet states have been determined in the B3LYP/6-311G(2d,2p) approximations. The Mulliken analysis and non-bonding orbital approach have been used in characterization of the studied compounds. It has been shown that the HOMO-LUMO transition of the studied compounds is observed in the range $23,900 \div 29,300 \text{ cm}^{-1}$ and in this excitation the π -electrons of phenyl ring are transferred to nitro group of pyridine ring. In such a transition the hydrazo-bridge should take part as a mediator. The luminescence of the studied hydrazo-compounds is weak, not measurable in the solid state but measurable in solution.

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1. Introduction

Pyridine does not exhibit luminescence in its liquid phase [1,2], but it was observed in the vapour state [3]. For azines that have the lowest excited singlet state S_1 of an (n, π^*) type, intense phosphorescence has been reported [4]. Weak $\pi^* \rightarrow n$ fluorescence has also been recorded for other azines, i.e. pyridazine, pyrimidine, pyrazine [5]. Symmetry allowed $n \rightarrow \pi^*$ transitions in pyridine and other N-heterocycles has been described as the result of asymmetry of the n-orbital of N-atom [6]. Although pyridine alone shows no luminescence, the fluorescence of mono(2,3 and 4)- and di(2,3; 3,4 and 2,6)-aminopyridines as well as 2-amino-6-picoline was detected and discussed in terms of their electronic structure and sequence of the excited states. It was stated that the fluorescence of these compounds strongly depends on the substitution place of the amino-group. For instance, 4-aminopyridine showed negligible

fluorescence probably due to (n, π^*) transitions. Other studied compounds were strong fluorophores, which was explained as a result of (π, π^*) nature of the lowest excited state. These studies clearly revealed pronounced effects of the substitution place and the type of substituents on the efficiency of the fluorescence of nitrogen containing heterocycles.

In our previous work [7] the excited states of several 2-alkylamino-(3 or 5)-methyl-4-nitropyridine derivatives in the solid state and alcoholic solutions were studied on the basis of their electronic absorption and emission spectra. The luminescence and its lifetimes were recorded at room and liquid helium temperature. The energy sequence of the singlet and triplet states were determined and compared to the results of DFT quantum chemical calculations. The present work is a continuation of the earlier studies. The electronic absorption and luminescence spectra of four phenylhydrazo-pyridine derivatives were measured and analysed in terms of DFT quantum chemical calculations. The vibrational properties of hydrazo-bridge bond in these compounds were reported in our previous papers [8,9]. Here the influence of the hydrazo-bond and a solvent on the electronic absorption properties of these compounds

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has been studied. Their non-bonding orbitals and electron densities have been determined to characterize electron character of the hydrazo-bond and pyridine and phenyl rings. The role of the hydrazo-bond in the depopulation of the excited states has been analysed.

The knowledge of the electronic structures of four studied isomers is very important for explanation of the spectroscopic behavior of these systems. They can be used as complexing lanthanide ions ligands enhancing their luminescence or they can be employed in various applications, e.g. as optical sensors in medicine.

2. Experimental

2.1. Characterization of the studied compounds

The studied in the present work hydrazo-compounds are specified in Fig. 1. Their syntheses were described in our earlier work [9].

2.2. Spectroscopic studies

Electronic absorption spectra of the studied compounds were measured in Nujol mulls and in *n*-heptane, ethanol, methanol, chloroform, water and acetonitrile using a JASCO V-570 UV/VIS spectrophotometer with the resolution of 0.5 nm. All the used solvents were spectral grade.

Emission spectra were measured by a highly sensitive spectrofluorometer NIR-VIS PTI (Photon Technology International) working in T-configuration and equipped with an InGaAs (above 1200 nm) detector and photon-counting system (range 200 ÷ 1000 nm).

2.3. Quantum chemical calculations

Calculations of the electronic energy states of the studied compounds were performed using the GAUSSIAN 03 programme package [10]. The starting geometry was optimized with the same method and procedure. The atomic basis set of different quality was used including the 6-311G(2d,2p) Gaussians with polarization functions. The results obtained from the *ab initio* TD DFT calculations with B3LYP/6-311G(2d,2p) density functional in the 'gas phase approximation' and in the solutions have been compared with the experimental data. The results of these calculations are presented in Table 1. The influence of the solvent polarity on the spectral parameters has been calculated using the polarizable continuum (PCM) model. The NBO calculations have been performed using the NBO program [11], implemented in the Gaussian 03 W package. The molecular orbital (MO) calculations were also performed for the studied compounds. The ChemCraft and

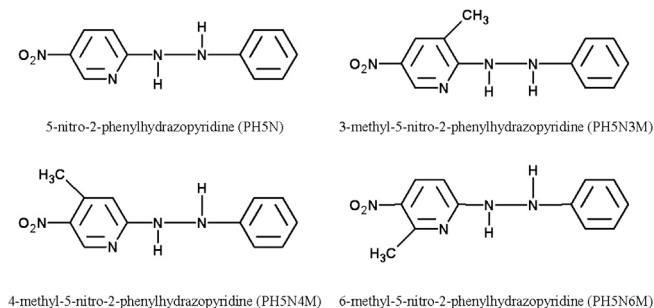


Fig. 1. Specification of the studied compounds.

Table 1

Selected geometrical parameters of the studied hydrazo compounds obtained from the structure optimisation.

| | PH5N | PH5N3M | PH5N4M | PH5N6M |
|---|--------|--------|--------|--------|
| | [Å] | | | |
| C2 _P -N _{HAP} | 1.368 | 1.373 | 1.375 | 1.376 |
| N _{HAP} -N _{HAB} | 1.384 | 1.373 | 1.399 | 1.402 |
| N _{HAB} -C1 _B | 1.411 | 1.391 | 1.418 | 1.412 |
| N _{HAP} -H _{HAP} | 1.005 | 1.008 | 1.007 | 1.008 |
| N _{HAB} -H _{HAB} | 1.011 | 1.008 | 1.012 | 1.013 |
| C(3 _P or 4 _P or 6 _P)-C _{CH3} | — | 1.496 | 1.504 | 1.501 |
| λC5 _P -N _{NO2} | 1.448 | 1.448 | 1.460 | 1.460 |
| | [°] | | | |
| N1 _P ...H _{HAB} -N _{HAB} | 97.63 | 68.32 | 100.46 | 102.95 |
| C2 _P -N _{HAP} -N _{HAB} | 120.74 | 120.00 | 120.43 | 120.17 |
| N _{HAP} -N _{HAB} -C1 _B | 116.69 | 118.48 | 116.78 | 116.51 |
| C2 _P -N _{HAP} -H _{HAP} | 117.01 | 116.29 | 116.39 | 115.53 |
| H _{HAB} -N _{HAB} -C1 _B | 111.41 | 116.12 | 111.49 | 111.71 |
| C2 _P -N _{HAP} -N _{HAB} -C1 _B | 99.03 | 114.29 | 104.18 | 107.99 |
| H _{HAP} -N _{HAP} -N _{HAB} -H _{HAB} | 118.81 | 76.62 | 121.06 | 122.83 |

GaussView graphical programs were used for visualization of the computed results [12,13].

3. Results and discussion

3.1. Molecular geometry of the studied compounds

Labelling of the atoms in the monomer and dimer structures of the studied compounds are presented in Fig. 2.

Table 1 lists their selected geometrical parameters, mainly those

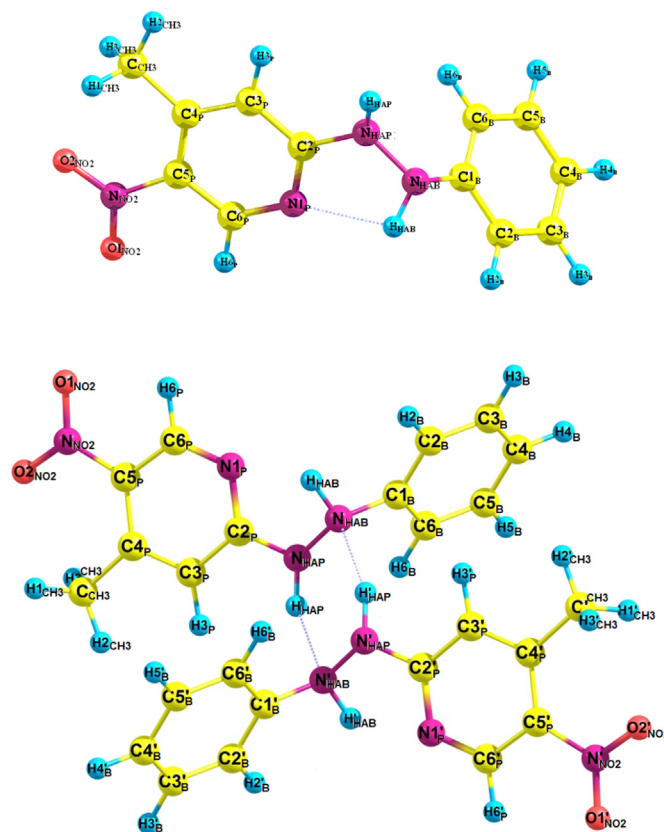


Fig. 2. Labelling of atoms in the structure of PH5N4M compound.

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