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# Acid–base properties of 3,5-dimethyl-1,7-diphenyl derivative of bis-pyrazolopyridine in non-aqueous solutions

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**Abstract**

Acid–base properties of 3,5-dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b;4′,3′-*e*]-pyridine (BPP) in the ground state and in the first excited singlet state were investigated in non-aqueous solutions. Absorption and stationary fluorescence spectroscopy, supersonic jet spectroscopy as well as the calculations of effective valence potentials were applied as methods. The sequence of the protonation of BPP nitrogen atoms in solutions and the formation of complexes with water in molecular beams were discussed.


*Keywords:* Bis-pyrazolopyridines; Acid–base properties; Fluorescence; Supersonic jet

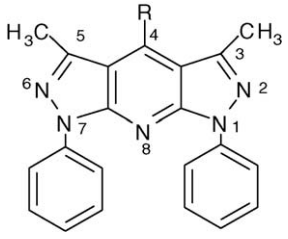
## 1. Introduction

3,5-Dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b;4′,3′-*e*]-pyridine (BPP) is the parent compound for numerous derivatives with valuable properties in the aspect of recognition and application.

The derivatives of BPP with (4′-*N*,*N*-alkylaminophenyl) in position 4 show a low lying highly dipolar charge-separated excited state, and are therefore promising candidates for efficient non-linear optical (NLO) materials.

Derivatives with various other substituents in position 4 showing intense fluorescence can be used as fluorescence standards and have found application as blue-green organic light-emitting diodes [1,2]. Some of BPP derivatives show biological activity and are considered as medicines [3].

The acid–base properties of four derivatives: DMA-DMPP, H-DMPP, $NO_2$-DMPP and $CH_3O$-DMPP (see Formulae 1) were investigated previously [4,5].




The donor–acceptor molecule, DMA-DMPP, has three different possible protonation centers and undergoes the protonation in step-by-step processes. The amino group is protonated as the first one in the ground as well as in the excited state. The question arises which nitrogen atom in heterocyclic subunit is protonated as the next one. The results of semi-empirical calculations [4] hinted at the protonation of pyridine nitrogen, but the prevention from such protonation due to steric hindrance of phenyls 1 and 7 was also mentioned [6]. On the other hand, the effective valence electron potentials hint to protonation of pyrazolic nitrogen in the molecule already protonated on the amino group [5]. The basic properties of *N*,*N*-dimethylamino group in DMA-DMPP practically do not change in the first excited singlet state, $S_1$. The basicity of the nitrogen protonated in the second step increases

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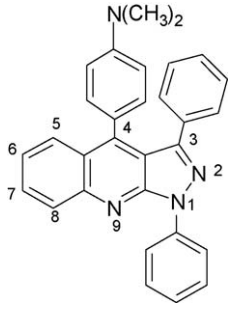
remarkably in the $S_1$ state. The protonation occurs much easier in acetonitrile solutions than in ethanolic ones.

The three other studied derivatives H-, $NO_2$- and $CH_3O$-DMPP, undergo protonation as it is in the case of the second step of DMA-DMPP.

In the present paper, we describe the results of the investigations of BPP acid–base properties in the ground state and in the $S_1$ state, which should be helpful in deeper understanding of the protolytic processes in the four compounds described in [4]. The comparison of the behaviour of BPP with that of the above mentioned compounds and first of all with that of DMA-DPPQ [7] (Formula 2) led to the assignation of protonation sequence in heterocyclic system.




The investigations were performed for non-aqueous solutions, i.e. in acetonitrile and ethanol as solvents, because of sparingly small solubility of BPP in water. Additionally, the clusters of BPP with water molecule were studied in a supersonic jet.

## 2. Materials, experimental and computation methods

BPP was synthesized and purified according to Brack [8]. The solvents and $HClO_4$ (72% w/w) were of the highest available quality and checked for impurities by means of absorption and fluorescence spectroscopy. Absorption spectra were measured with a Specord M 500 spectrophotometer. Fluorescence spectra and fluorescence excitation spectra were measured with a Kontron SFM 25 spectrofluorimeter.

All spectra of jet-cooled BPP were obtained with a home-built jet spectrometer. The sample was heated to 190 °C and injected through a 500 μm pulsed nozzle (General Valve Series 9) into the vacuum chamber evacuated by a turbomolecular pump (Leybold Turbovac 600C). Helium was used as a carrier gas. A home-built dye laser with spectral width of <0.2 $cm^{-1}$, pumped by the 3rd harmonic of a Nd:YAG laser (Surelite I-10) was used for fluorescence excitation. Total fluorescence was collected by a toroidal mirror and imaged onto a cooled photomultiplier (Hamamatsu R). The signal from the photomultiplier was digitized by a digital oscilloscope (Le Croy 9310) and stored in a personal computer. Molecular clusters of BPP and water were formed in the jet by passing the carrier gas though the reservoir with the solvent. The amount of the solvent added into the carrier gas and the stoichiometry of the complexes formed were controlled by changing the reservoir temperature.

To estimate the reactivities of different aza-atoms, we calculated the Spanget-Larsen's indexes of reactivity [2,9–11], called effective potential energies of valence electrons ($\mu^A$ – for μ orbital of A atom) or effective valence potentials. These potentials can be defined in terms of atomic charges and interactions between atoms:

$$W_\mu^A = W_\mu^A(q_A) + \sum_{B\neq A} W_\mu^A(q_B) \quad (1)$$

$$W_\mu^A(q_A) = -(a + bq_A)^{3/2} \quad (2)$$

$$W_\mu^A(q_B) = \gamma_{AB}(q_B - Z'_B) \quad (3)$$

where $q_A$ and $q_B$ are total electron populations on A and B atoms. The $\gamma_{AB}$ is the Coulomb integral representing repulsing interactions between valence electrons of A and B atoms. The $a$ and $b$ constants were derived from the dependence of ionization potentials on cation and anion charges. $Z'_B$ denotes the number of valence electrons in the neutral atom B.

The ability of aza-atoms to attach a proton can be estimated from effective potentials calculated in this way. Higher positive values of $W_\mu^A$ correspond to a higher basicity of the A atom and to more nucleophilic nature of the appropriate region of the molecule. We calculated $W_\mu^A$ values only for nitrogen atoms in the heterocyclic system because this method is not good enough to estimate the basicity of N-atoms of the amino group.

Calculations of potentials were based on molecular geometries calculated by the AM1 method and charge densities were calculated by the INDO/S method.

The molecular geometries and the values of heats of formation for protonated molecules were obtained within AM1 method.

## 3. Results

### 3.1. Stationary absorption and fluorescence spectra

The absorption spectra of BPP in acetonitrile as solvent with different amounts of $HClO_4$ are shown in Fig. 1.

Upon increasing of acid concentration, the new long wavelength band peaking at 26 300 $cm^{-1}$ appears, accompanied by the changes in the short wavelength range. The band reaches its maximal absorbance at $[HClO_4] \cong 6 \times 10^{-2}$ M. Further addition of acid does not change this band, but causes some changes at the short wavelength range, up to $4 \times 10^{-1}$ M of acid concentration, Fig. 1c. The isosbestic points hint at the equilibrium between BPP molecule and its protonated forms.

In acidified ethanolic solutions, the changes of absorption spectra of BPP are rather small (Fig. 2).

BPP emits a strong fluorescence with the maximum at 22 600 $cm^{-1}$ in acetonitrile and 22 500 $cm^{-1}$ in ethanol. This band is effectively quenched by acid (Fig. 3a and b) and disappears totally when $[HClO_4] > 1.0 \times 10^{-2}$ M in acetonitrile solution, Fig. 3b.

The quenching of BPP fluorescence correlates with the increase of the new long wavelength absorption band, Fig. 4. The half values of the absorbance and fluorescence are reached at similar acid concentration (log $[HClO_4]$ in range −3.0 to −3.4). The disappearing of the fluorescence band