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# Solvent effect and quantum chemical calculations of the electron energy levels for nitro derivatives of 2-(*N*-methylamino)-picolines

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#### Abstract

Electronic absorption spectra of 2-(*N*-methylamino)-3-methyl-4-nitropyridine (M3M4NP), 2-(*N*-methylamino)-5-methyl-4-nitropyridine (M5M4NP), 2-(*N*-methylamino)-3-methyl-5-nitropyridine (M3M5NP) and 2-(*N*-methylamino)-5-methyl-3-nitropyridine (M5M3NP) in the ethyl alcohol, acetonitrile and *n*-heptane solution as well as solid state have been measured at room temperature. The influence of the solvent and substitution on polar and non-polar properties has been discussed. The results obtained by the ab initio TD DFT quantum calculations using MPW1PW91 and B3LYP functional and 6-31G(d,p) basis have been compared with that of experimental values.

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Keywords: Electronic absorption spectra; Quantum chemistry calculations; Solvent effects; Substituted picolines

### 1. Introduction

An increased interest in the structure of pyridine derivatives, observed in recent years, is related to their potential use as non-linear optical materials [1] and as photochemicals [2-6]. In particular, some of the crystals could be used as frequency convectors from NIR to visible region. The UV spectra of substituted pyridines, such as aminopyridines [7-9], nitropyridines [9] and aminonitropyridines [9-14] as well as methyl substituted aminopyridines [15,16] and 4-substituted 2-nitroaniline [17] have been studied. The ultraviolet absorption spectra of the amino-, cationic- and imino-forms of some monocyclic aminoazines have been measured in aqueous solution as well as the spectra of amines in water, ethanol and cyclohexane solution [7]. The UV spectra of 2-amino-5nitropyridine were studied in polar and non-polar solvents [10]. 2-Amino-5-nitropyridines, in which interaction between the nitro and amino groups through the  $\pi$ -electron system is the main factor determining their electronic

structure and conformation, are of special interest. Equally interesting are 2-amino-3-nitropyridines where, besides strong conjugation, also the intramolecular hydrogen bond between the nitro and amino groups is an important structural element.

It is a well-known experimental fact that the spectrum of a substance in a solution is changed with respect to its spectrum in vapour phase. In many cases the general shape of the absorption spectrum is unaltered and the main effect is a shift of various absorption bands. The shifts of absorption spectra bands are related to the solute–solvent interactions.

Solvent effects on physical or chemical processes are usually studied by means of empirical solvent parameters and these parameters have also been measured for solvent mixtures [18]. The UV/VIS absorption spectra of 1-methyl-4-[4-aminostyryl]pyridinum iodide (M–NH<sub>2</sub>) were measured in 11 solvents of different polarity [19]. The dramatic shifts in electronic absorption spectra observed on going from pyridine—21,413 cm<sup>-1</sup> to water—24,876 cm<sup>-1</sup> was explained as a result of the solute-solvent interaction. The electronic transition energy was increasing with increasing solvent polarity. The authors proposed that one of the main factors causing the solvatochromic behaviour is the hydrogen-bonding interaction between the M–NH<sub>2</sub> lone

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pair of electrons and the hydrogen bond donor solvent molecules. In the hydrogen bond donor solvents, such as water and alcohol, the interaction stabilizes the benzenoid structure. In the presence of the more polar solvent the probability of the conjugation increases.

Another example of solvent effect studies is comparison of absorption spectra of 2-(2'-hydroxyphenyl)1H-imidazo[4,5-c]pyridine in different solvents and mixtures of binary solvents [20].

The experimental and calculated absorption spectra have also been compared for *p*-nitroaniline [21]. The striking feature of these spectra is the appearance of partial electron migration in the molecule. The authors assigned the band near 380 nm (26,316 cm<sup>-1</sup>) to the charge transfer transition from the nitrogen non-bonding orbital of the amino group to vacant orbital of the nitro group. The experimental and theoretical results in terms of the band gap energy are in good agreement.

The solvatochromic behaviour of *o*-, *m*-, *p*-nitroanilines and several *N*-alkyl-*o*-nitroaniline derivatrives was also studied [22,23]. This behaviour was compared for the longest wavelength absorption band measured for several pure solvents and solvent mixtures.

A large number of computational studies have been performed in order to identify the electronic states of pyridine. Several theoretical models have been employed starting from the Hartree–Fock and Moller–Plesset perturbation theories to the time-dependent density-functional studies. All these methods and results have been reviewed by Zheng-Li Cai and Reimers [24]. The values of  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  singlet energy transitions and oscillator strengths for the two lowest  $\pi \rightarrow \pi^*$  singlet states of the 2-aminopyridine and 3-, 4-, 5- and 6-methyl-2-aminopyridine were investigated employing the CNDO-CI procedure [16].

The localized-orbital model with configuration interaction, including the inductive effect of the substituent, has been used to calculate transition energies, oscillator strengths and dipole moments of  $\pi \rightarrow \pi^*$  bands in the electronic spectra of amino-, nitro- and aminonitropyridines [9]. In the case of amino- and nitropyridines the comparison between theoretical transition energies and experimental frequency of bands, reveals a good agreement. In aminonitropyridines agreement between the calculated and experimental energies, particularly of the first band, is not satisfactory. Theoretical values exceed experimental data in hexane (or cyclohexane) by 4032–7257 cm<sup>-1</sup>. The theoretical overestimation was observed by Godfrey and Murrell [25] for nitroanilines.

The dependence of the calculated energies on the DFT basis set used has been also noticed by us for the excited states of pyridine derivatives. The comparison of the results obtained for these systems using the ZINDO, B3LYP/6-31G, B3LYP/Huzinaga, MPW1PW91/6-31G, MPW1PW91/ Huzinaga and MPW1PW91/6-31G(d,p) approaches was made in our previous papers [26,27].

### 2. Experimental and computational section

### 2.1. Synthesis of 2-(N-methylamino)-3-(or 5)-methyl-4nitropyridines

2-(*N*-methylamino)-3-(or 5)-methyl-4-nitropyridines have been obtained by N-deoxygenation of 2-(*N*-methylamino)-3-(or 5)-methyl-4-nitropyridine N-oxides [28]. A sample of 4 g of 2-(*N*-methylamino)-3-methyl-4-nitropyridine N-oxide was dissolved in 40 ml of chloroform, then 8 ml of PCl<sub>3</sub> was added and the mixture was refluxed for 1 h. The reaction mixture was next evaporated to dryness. After distilling off the chloroform, adding ice and neutralization with potassium carbonate, the residue was extracted with chloroform. Chloroform was removed and the residue to give M3M4NP recrystallized from water. The M5M4NP was prepared in the same way. The composition was established by microanalysis giving the following stoichiometry:

M3M4NP; found: C—50,71, H—5,38, N—25,29 wt%; calculated: C—50,30, H—5,43, N—25,14 M5M4NP; found: C—50,06, H—5,26, N—25,15 wt%; calculated: C—50,30, H—5,43, N—25,14

### 2.2. Synthesis of 2-(N-methylamino)-3-(or 5)-methyl-4nitropyridine N-oxides

A mixture containing 5 g of 2-chloro-3-(or 5)-methyl-4nitropyridine N-oxide and 20 ml of 30% methylamine solution in ethanol was refluxed for 5 h. After distilling off ethanol and adding water the precipitate was filtered off and re-crystallised from water to give 2-(*N*-methylamino)-3methyl-4-nitropyridine N-oxides (M3M4NPO) or 2-(*N*methylamino)-5-methyl-4-nitropyridine N-oxides (M5M4NPO). The composition was established by microanalysis giving the following stoichiometry:

M3M4NPO; found: C—46,17, H—4,79, N—23,21 wt%; calculated: C—45,90, H—4,95, N—22,94 M5M4NPO; found: C—45,78, H—4,81, N—23,17 wt%; calculated: C—45,90, H—4,95, N—22,94

The M3M4NP and M5M4NP samples have been obtained in the polycrystalline state.

## 2.3. Synthesis of 2-(N-methylamino)-3-(or 5)-methyl-5-(or 3)-nitropyridine

2-(*N*-methylamino)-3-(or 5)-methyl-5-(or 3)-nitropyridines have been obtained by methylamination of 2-chloro-3-(or 5)-methyl-5-(or 3)-nitropyridine [29]. A sample of 5 g of 2-chloro-3-(or 5)-methyl-5-(or 3)-nitropyridine was dissolved in 55 ml of ethanol. Then 5.7 g of 30% methylamine solution in ethanol was added and mixture was refluxed for 1 h. After 1 h the reaction mixture was cooled and the precipitate was filtered off and re-crystallised from methanol. The composition was established by microanalysis giving the following stoichiometry:

M3M5NP; found: C—50,11, H—5,55, N—25,00 wt%; calculated: C—0,30, H—5,43, N—25,14 M5M3NP; found: C—50,12, H—5,60, N—25,20 wt%; calculated: C—50,30, H—5,43, N—25,14

### 3. Spectroscopic studies

The systems under consideration have been studied using electronic absorption spectroscopy. The spectra of the samples in the Nujol mulls and dissolved in the *n*-heptane, ethanol and acetonitrile were measured using JASCO V-570 UV/VIS spectrophotometer with the resolution of 0.5 nm. All the solvents used were of spectral grade.

The ORIGIN 5.0 software [30] has been used to deconvolute the experimental spectra of studied compounds. The Gaussian deconvolutions of the experimental absorption spectra in different media are presented in Tables 1–4. The errors of the Gaussian deconvolution ( $\chi^2$ ) for particular spectra ranged from  $10^{-4}$  to  $10^{-6}$ .

### 4. Quantum chemical calculations

The calculations of the electronic energy states for molecules under investigation have been performed using the GAUSSIAN 98W package of programs [31]. The starting geometry was optimized with the same method and procedure. The atomic basis set of different quality was used including the 6-31G(d,p) Gaussians with polarization functions. The results obtained from the ab initio TD DFT calculations with MPW1PW91 and B3LYP density functional in the 'gas phase approximation' and in the media have been compared with the experimental data. The results of these calculations are presented in Tables 1–4.

### 5. Absorption spectra

The absorption spectra of the M3M4NP, M5M4NP, M3M5NP and M5M3NP were measured in three solvents of different polarity: *n*-heptane ( $\mu$ =0 D), ethanol ( $\mu$ =1.69 D), acetonitrile ( $\mu$ =3.92 D) [32] and in the Nujol mull. As shown in Figs. 1–4, the solvent polarity influences strongly the position of the electronic absorption maxima. The comparison of the calculated and experimental data is presented in Tables 1–4.

The experimental absorption spectra of M5M4NP in all solutions, in the region 20,000–50,000 cm<sup>-1</sup>, consist of two bands at 42,553–41,493 and 26,596–25,445 cm<sup>-1</sup> (Fig. 2). In the case of M3M4NP, the first band is observed in the 28,409–27,100 cm<sup>-1</sup> region and the second one in

the 42,553–41,493 cm<sup>-1</sup> region. Moreover, the third band for M3M4NP appears at 49,505 or at 49,261 cm<sup>-1</sup>, in ethanol and acetonitrile solution, respectively (Fig. 1). All the bands are sensitive to the nature of the solvent and are slightly red shifted with increasing polarity and hydrogen bonding ability of the solvent. The absorption spectra of these two isomers measured in Nujol mull, *n*-heptane, ethanol and acetonitrile solution are similar.

The absorption spectra of M5M3NP exhibit the triplet of bands in the region 20,000–50,000 cm<sup>-1</sup>. The bands appear at 44,053–43,860, 37,453–37,037 and 24,231–23,310 cm<sup>-1</sup> (Fig. 4). The 43,860–44,053 cm<sup>-1</sup> band is not sensitive to the nature of the solvent, but the 37,000 cm<sup>-1</sup> band behaves in a different way. On passing from *n*-heptane to ethanol solution it shows a weak red-shift  $(37,175 \rightarrow 37,037 \text{ cm}^{-1})$  whereas on passing from *n*-heptane and ethanol to acetonitrile a blue-shift is observed  $(37,170 \rightarrow 37,450 \text{ cm}^{-1})$ .

The absorption spectrum of M3M5NP measured in Nujol mull differs from the spectra in solutions. The spectra in solutions consist of four bands at 50,000-49,504, 45,545-44,444, 30,488-33,333 sh and 29,240-27,248 cm<sup>-1</sup>, whereas, the spectrum in Nujol mull is more complicated (Fig. 3). Significant differences between absorption spectra of M3M5NP in solutions and in a solid state are observed. This behaviour can result from interactions between the molecules in a solid state. The solid phase effect is due to the engagement of the -NHTAB group in the intermolecular hydrogen bond with the nitro group of the neighbouring molecule. The structural studies of 2-amino-5-nitropyridine, 2-amino-3-nitropyridine and 2-amino-4-nitropyridine have been previously published [33–35]. It has been shown that molecules of 2-amino-5-nitropyridine are connected into two-dimensional network by N-H···O, C-H···O and C-H···N hydrogen bonds. However, the most important are the N–H $\cdots$ O hydrogen bond interactions [35].

It has been observed that m- and p-nitroanilines form dimers in CCl<sub>4</sub> and CHCl<sub>3</sub> solutions by hydrogen bonding between the amino hydrogen of one molecule and the nitro group of the other one. This behaviour is distinct from that observed for o-nitroaniline, where the intramolecular hydrogen bond reduces the possibility of intermolecular interaction [36]. However, the results of the UV/VIS studies showed that the intramolecular hydrogen bond in o-nitroaniline and N-methyl-o-nitroaniline does not break to form intermolecular hydrogen bonds of the strength similar to that in N-methylpyrrolidin-2 [17].

The absorption maxima of the first bands are observed at the largest wavenumbers in *n*-heptane and smaller ones in the ethanol and acetonitrile solution. The first band observed in the range 24,000–29,000 cm<sup>-1</sup> is characterized by a large contribution of the electron transfer from the highest occupied to the lowest vacant molecular orbitals (MO). Like for other pyridine derivatives with donor (–NHCH<sub>3</sub>) and acceptor (–NO<sub>2</sub>) groups, the charge transfer (CT) band in the nitro derivatives of 2-methylaminopicolines is strongly solvent dependent. The first band for isomers

Comparison of the calculated and experimental excitation energies  $(cm^{-1})$  and oscillator strengths for 2-(*N*-methylamino)-3-methyl-4-nitropyridine in Nujol mull, *n*-heptane, ethanol and acetonitrile solution

$ \frac{deconvolution}{2} state \\ \hline MPW IPW91/6-31G(d,p) \\ \hline sym form \\ sym form$	Solvent	Exp.	Gaussian	Singlet	Calculated excitation energies								
	Nujol		deconvolution	state	e MPW1PW91/6-31G(d,p) B3LYP /6-31G(	6-31G(d,p)	l,p)						
$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$					syn form		anti form	I	syn form		anti form		
28,903 S- 31,316 0.006 31,540 0.008 30,239 0.008   33,571 S. 36,452 0.001 36,924 0.001 34,889 0.001 35,336 0.001   36,311 S. 41,040 0.022 41,276 0.046 38,904 0.024 90,714 0.042   37,769 S. 42,317 0.027 42,689 0.036 40,591 0.015 44,420 0.032   42,017 42,356 S. 45,739 0.171 48,522 0.011 44,387 0.170 44,944 0.004   43,156 S. 46,577 0.171 48,262 0.216 44,980 0.033 49,040 0.031   n-heptane 28,409 27,372 S. 26,908 0.030 25,624 0.027 24,866 0.023 23,618 0.020   36,433 S. 36,447 0.001 36,947 38,238 0.001 35,340 0.001   36,416		27,100	27,325	<b>S</b> <sub>1</sub>	27,622	0.032	26,427	0.028	25,626	0.025	24,462	0.022	
30,500 S <sub>1</sub> 34,238 0.002 34,306 0.002 32,668 0.003 32,605 0.002   36,311 S <sub>1</sub> 41,040 0.022 41,276 0.046 38,891 0.021 39,714 0.002   37,769 S <sub>6</sub> 42,372 0.027 42,689 0.036 49,591 0.015 40,420 0.032   42,017 42,356 S <sub>8</sub> 46,382 0.014 46,432 0.011 44,307 0.170 44,944 0.004   52,457 S <sub>10</sub> 50,378 0.032 51,229 0.023 43,664 0.023 23,618 0.001   25,457 S <sub>10</sub> 50,378 0.032 51,229 0.023 43,664 0.023 23,618 0.001   36,543 S <sub>4</sub> 36,437 0.001 34,928 0.021 32,360 0.031 32,360 0.031 32,360 0.031 32,360 0.031 32,360 0.031 32,366 0.001 35,386 0.001 35,386 <td></td> <td></td> <td>28,903</td> <td><math>S_2</math></td> <td>31,316</td> <td>0.006</td> <td>31,540</td> <td>0.008</td> <td>30,037</td> <td>0.006</td> <td>30,239</td> <td>0.008</td>			28,903	$S_2$	31,316	0.006	31,540	0.008	30,037	0.006	30,239	0.008	
33,571 S4 36,452 0.001 36,924 0.001 34,889 0.001 53,36 0.001   37,769 S6 42,372 0.027 42,689 0.036 40,591 0.015 40,420 0.032   40,006 S7 45,739 0.173 46,422 0.011 44,307 0.170 44,443 0.014 43,05 0.040   42,017 42,645 S8 46,577 0.171 48,622 0.023 44,48 0.024 40,140 0.030   n-heptane 28,409 27,372 S1 25,098 0.030 25,624 0.022 42,616 0.003 32,161 0.003 34,012 0.002 32,416 0.003 34,022 0.001 35,336 0.003 32,057 0.006 31,661 0.003 32,050 0.003 32,050 0.003 32,050 0.003 32,050 0.003 32,050 0.004 33,934 0.005 31,175 0.004 33,934 0.005 31,175 <td></td> <td></td> <td>30,500</td> <td><b>S</b><sub>3</sub></td> <td>34,238</td> <td>0.002</td> <td>34,306</td> <td>0.002</td> <td>32,686</td> <td>0.003</td> <td>32,605</td> <td>0.002</td>			30,500	<b>S</b> <sub>3</sub>	34,238	0.002	34,306	0.002	32,686	0.003	32,605	0.002	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			33,571	$S_4$	36,452	0.001	36,924	0.001	34,889	0.001	35,336	0.001	
37,769 S <sub>6</sub> 42,372 0.027 42,689 0.036 0.051 40,900 0.032   42,017 42,356 S <sub>8</sub> 46,382 0.046 46,970 0.232 44,488 0.125 45,559 0.040   43,156 S <sub>9</sub> 46,577 0.171 48,262 0.216 45,090 0.081 46,104 0.33   n-heptane 28,409 27,372 S <sub>1</sub> 26,908 0.030 25,624 0.022 42,466 0.023 34,01 0.003 32,678 0.030 34,012 0.003 32,646 0.003 32,646 0.003 32,646 0.003 32,646 0.003 32,646 0.003 32,400 0.001 35,346 0.001 35,346 0.001 35,346 0.001 35,346 0.001 35,346 0.001 35,340 0.001 34,023 0.011 45,99 0.022 44,141 0.006 34,64 0.023 44,141 0.022 44,141 0.014 39,818 0.005			36,311	S <sub>5</sub>	41,040	0.022	41,276	0.046	38,904	0.024	39,714	0.042	
$ \begin{array}{c} + 0.906 & S_7 & 45.739 & 0.173 & 46.432 & 0.011 & 44.307 & 0.170 & 44.944 & 0.004 \\ 42.017 & 42.356 & S_8 & 46.382 & 0.046 & 46.970 & 0.232 & 44.86 & 0.125 & 45.579 & 0.040 \\ 3.156 & S_9 & 46.577 & 0.171 & 48.262 & 0.216 & 45.090 & 0.081 & 46.104 & 0.383 \\ 52.457 & S_{10} & 50.378 & 0.032 & 51.229 & 0.023 & 48.664 & 0.023 & 49.140 & 0.001 \\ 29.632 & S_2 & 31.460 & 0.006 & 31.661 & 0.008 & 30.175 & 0.006 & 30.340 & 0.008 \\ 32.759 & S_3 & 34.113 & 0.003 & 34.102 & 0.002 & 32.461 & 0.003 & 32.300 & 0.003 \\ 36.343 & S_4 & 36.437 & 0.001 & 36.907 & 0.001 & 34.928 & 0.001 & 35.386 & 0.001 \\ 36.343 & S_4 & 36.437 & 0.001 & 36.907 & 0.001 & 34.928 & 0.001 & 39.818 & 0.026 \\ 41.655 & S_7 & 45.570 & 0.210 & 46.432 & 0.021 & 43.988 & 0.122 & 44.944 & 0.026 \\ 41.655 & S_7 & 45.570 & 0.210 & 46.432 & 0.021 & 43.988 & 0.122 & 44.944 & 0.006 \\ 43.682 & S_8 & 46.73 & 0.178 & 46.737 & 0.178 & 44.181 & 0.213 & 45.086 & 0.035 \\ 41.655 & S_7 & 45.570 & 0.210 & 46.432 & 0.021 & 43.988 & 0.122 & 40.944 & 0.006 \\ 43.682 & S_8 & 47.664 & 0.265 & 47.664 & 0.264 & 45.122 & 0.045 & 45.829 & 0.393 \\ 51.102 & S_{10} & 51.229 & 0.002 & 51.239 & 0.002 & 48.787 & 0.001 & 49.044 & 0.000 \\ 30.872 & S_1 & 33.852 & 0.005 & 33.714 & 0.005 & 30.631 & 0.006 & 31.847 & 0.007 \\ 30.872 & S_1 & 33.852 & 0.005 & 33.714 & 0.005 & 30.631 & 0.006 & 31.847 & 0.007 \\ 34.119 & S_4 & 36.649 & 0.01 & 37.160 & 0.001 & 35.211 & 0.01 & 35.714 & 0.000 \\ 41.493 & 35.183 & S_8 & 45.106 & 0.311 & 49.785 & 0.034 & 42.735 & 0.100 & 43.668 & 0.025 \\ 49.505 & 40.716 & S_7 & 44.926 & 0.087 & 45.785 & 0.034 & 42.735 & 0.100 & 45.551 & 0.175 \\ 50.119 & S_{10} & 51.046 & 0.002 & 51.203 & 0.004 & 45.66 & 0.011 & 35.637 & 0.000 \\ 37.740 & S_8 & 45.920 & 0.022 & 42.360 & 0.021 & 45.980 & 0.021 & 45.240 & 0.019 \\ 43.334 & S_9 & 46.926 & 0.001 & 37.160 & 0.004 & 45.652 & 0.103 & 43.668 & 0.086 \\ 41.94 & 3.039 & S_5 & 51.102 & 0.002 & 51.036 & 0.001 & 45.555 & 0.137 \\ 41.94 & 40.820 & S_7 & 44.926 & 0.031 & 40.243 & 0.49 & 71.453 & 0.002 & 31.848 & 0.001 \\ 37.740 & S_8 & 45.$			37,769	S <sub>6</sub>	42,372	0.027	42,689	0.036	40,591	0.015	40,420	0.032	
$ \begin{array}{c} 42,017 & 42,356 & S_8 & 46,382 & 0.046 & 46,970 & 0.232 & 44,488 & 0.125 & 45,579 & 0.040 \\ 43,156 & S_9 & 46,577 & 0.711 & 48,262 & 0.216 & 45,090 & 0.081 & 46,104 & 0.383 \\ 52,457 & S_{10} & 50,378 & 0.032 & 51,229 & 0.023 & 48,664 & 0.023 & 23,618 & 0.020 \\ 32,759 & S_2 & 31,460 & 0.006 & 31,661 & 0.008 & 30,175 & 0.006 & 30,340 & 0.008 \\ 32,759 & S_3 & 34,113 & 0.003 & 34,102 & 0.002 & 32,461 & 0.003 & 32,300 & 0.003 \\ 36,343 & S_4 & 36,437 & 0.001 & 36,907 & 0.001 & 34,928 & 0.001 & 35,386 & 0.001 \\ 41,655 & S_7 & 45,70 & 0.210 & 46,342 & 0.021 & 43,988 & 0.122 & 44,944 & 0.006 \\ 43,682 & S_8 & 46,773 & 0.178 & 46,773 & 0.178 & 44,181 & 0.213 & 45,086 & 0.035 \\ 45,740 & S_9 & 47,664 & 0.226 & 47,664 & 0.264 & 45,122 & 0.045 & 45,29 & 0.393 \\ 45,740 & S_9 & 47,664 & 0.265 & 47,664 & 0.264 & 45,122 & 0.045 & 45,29 & 0.393 \\ 45,740 & S_9 & 47,664 & 0.265 & 47,664 & 0.264 & 45,122 & 0.045 & 45,29 & 0.393 \\ 45,740 & S_9 & 47,664 & 0.265 & 47,664 & 0.264 & 45,122 & 0.045 & 45,29 & 0.393 \\ 45,740 & S_9 & 47,664 & 0.265 & 47,664 & 0.265 & 10,065 & 30,487 & 0.001 & 49,044 & 0.000 \\ 27,322 & 25,912 & S_1 & 25,114 & 0.007 & 23,452 & 0.024 & 45,78 & 0.01 & 49,044 & 0.000 \\ 30,872 & S_3 & 33,852 & 0.005 & 33,714 & 0.005 & 32,051 & 0.006 & 31,847 & 0.007 \\ 34,119 & S_4 & 36,649 & 0.011 & 37,160 & 0.001 & 35,211 & 0.001 & 35,714 & 0.006 \\ 30,872 & S_3 & 31,874 & 0.006 & 31,967 & 0.008 & 30,581 & 0.005 & 30,487 & 0.004 \\ 43,334 & S_9 & 46,926 & 0.087 & 45,785 & 0.034 & 42,785 & 0.104 & 45,656 & 0.017 \\ 44,333 & S_9 & 46,926 & 0.087 & 45,785 & 0.034 & 42,785 & 0.016 & 38,610 & 0.025 \\ 49,55 & 40,716 & S_7 & 44,926 & 0.087 & 45,785 & 0.034 & 42,785 & 0.004 & 45,545 & 0.175 \\ 50,119 & S_6 & 41,533 & 0.018 & 46,266 & 0.027 & 39,378 & 0.001 & 35,377 & 0.000 \\ 37,740 & S_5 & 39,662 & 0.023 & 42,366 & 0.027 & 39,682 & 0.013 & 34,898 & 0.005 \\ 39,075 & S_6 & 41,533 & 0.018 & 41,235 & 0.027 & 39,682 & 0.013 & 34,898 & 0.001 \\ 41,494 & 40,820 & S_7 & 45,310 & 0.198 & 46,266 & 0.071 & 43,290 & 0.130 & 44,170 & 0.072 \\ 40,687$			40,906	<b>S</b> <sub>7</sub>	45,739	0.173	46,432	0.011	44,307	0.170	44,944	0.004	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		42,017	42,356	S <sub>8</sub>	46,382	0.046	46,970	0.232	44,488	0.125	45,579	0.040	
$ \begin{array}{c} 1.4 \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$			43,156	<b>S</b> <sub>9</sub>	46,577	0.171	48,262	0.216	45,090	0.081	46,104	0.383	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $			52,457	S <sub>10</sub>	50,378	0.032	51,229	0.023	48,664	0.023	49,140	0.001	
$ \begin{array}{c} 29,632 \\ 32,759 \\ 33,343 \\ 33,343 \\ 33,413 \\ 33,413 \\ 33,413 \\ 33,413 \\ 33,413 \\ 33,416 \\ 42,553 \\ 41,137 \\ 56 \\ 42,553 \\ 41,137 \\ 56 \\ 42,553 \\ 41,137 \\ 56 \\ 42,553 \\ 41,137 \\ 56 \\ 42,007 \\ 43,682 \\ 45,740 \\ 59 \\ 45,740 \\ 50 \\ 45,740 \\ 59 \\ 45,740 \\ 50 \\ 45,740 \\ 50 \\ 45,740 \\ 50 \\ 45,740 \\ 50 \\ 45,740 \\ 50 \\ 45,740 \\ 50 \\ 45,740 \\ 50 \\ 45,740 \\ 45,850 \\ 1000 \\ 51,229 \\ 0002 \\ 51,229 \\ 0002 \\ 48,780 \\ 0001 \\ 35,714 \\ 0000 \\ 31,871 \\ 0000 \\ 33,714 \\ 0001 \\ 35,871 \\ 0001 \\ 35,810 \\ 0001 \\ 3$	<i>n</i> -heptane	28,409	27,372	$S_1$	26,908	0.030	25,624	0.027	24,866	0.023	23,618	0.020	
32,759 S <sub>3</sub> 34,113 0.003 34,102 0.002 32,416 0.003 32,300 0.003   36,343 S <sub>4</sub> 36,437 0.001 36,907 0.001 34,928 0.001 35,386 0.001   42,553 41,137 S <sub>6</sub> 42,007 0.022 42,110 0.003 40,230 0.014 39,818 0.026   41,655 S <sub>7</sub> 45,570 0.210 46,432 0.021 43,998 0.122 44,944 0.006   43,682 S <sub>8</sub> 46,6773 0.178 46,773 0.178 44,181 0.213 45,868 0.001 45,086 0.035   45,740 S <sub>9</sub> 47,664 0.265 47,664 0.264 45,122 0.044 0.000   28,009 S <sub>2</sub> 31,874 0.006 31,967 0.008 30,581 0.005 31,447 0.006   28,009 S <sub>2</sub> 31,874 0.006 31,976 0.008 30,581 0.005 30,487			29,632	$S_2$	31,460	0.006	31,661	0.008	30,175	0.006	30,340	0.008	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			32,759	S <sub>3</sub>	34,113	0.003	34,102	0.002	32,461	0.003	32,300	0.003	
$ \begin{array}{ccccc} & 38,416 & S_5 & 40,464 & 0.023 & 40,888 & 0.047 & 38,283 & 0.023 & 39,324 & 0.045 \\ 42,553 & 41,137 & S_6 & 42,007 & 0.022 & 42,110 & 0.033 & 40,230 & 0.014 & 39,818 & 0.026 \\ 43,682 & S_8 & 46,773 & 0.178 & 46,773 & 0.178 & 44,181 & 0.213 & 45,086 & 0.035 \\ 45,740 & S_9 & 47,664 & 0.265 & 47,664 & 0.264 & 45,122 & 0.045 & 45,829 & 0.393 \\ 51,102 & S_{10} & 51,229 & 0.002 & 51,229 & 0.002 & 48,787 & 0.001 & 49,044 & 0.000 \\ 30,872 & S_3 & 33,852 & 0.005 & 33,714 & 0.005 & 32,051 & 0.006 & 31,847 & 0.007 \\ 34,119 & S_4 & 36,649 & 0.001 & 37,116 & 0.001 & 35,211 & 0.001 & 35,714 & 0.007 \\ 34,119 & S_4 & 36,649 & 0.001 & 37,160 & 0.001 & 35,715 & 0.017 & 38,023 & 0.038 \\ 42,338 & S_8 & 45,106 & 0.311 & 46,533 & 0.432 & 43,859 & 0.247 & 45,249 & 0.194 \\ 43,334 & S_9 & 46,926 & 0.008 & 46,338 & 0.016 & 43,668 & 0.086 \\ 42,338 & S_8 & 45,106 & 0.311 & 46,533 & 0.432 & 43,859 & 0.247 & 45,249 & 0.194 \\ 43,334 & S_9 & 46,926 & 0.008 & 46,338 & 0.016 & 45,662 & 0.010 & 45,655 & 0.175 \\ 50,119 & S_{10} & 51,046 & 0.025 & 23,809 & 0.021 & 22,292 & 0.019 \\ 36,520 & S_4 & 36,500 & 0.004 & 31,871 & 0.008 & 30,395 & 0.005 & 30,404 & 0.007 \\ 37,740 & S_5 & 33,600 & 0.004 & 33,781 & 0.003 & 32,154 & 0.000 & 45,745 & 0.019 \\ 41,494 & 40,820 & S_7 & 45,310 & 0.198 & 46,256 & 0.071 & 43,290 & 0.130 & 44,170 & 0.072 \\ 42,960 & S_8 & 45,555 & 0.020 & 45,818 & 0.004 & 43,280 & 0.004 & 43,743 & 0.020 \\ 41,494 & 40,820 & S_7 & 45,310 & 0.198 & 46,256 & 0.071 & 43,290 & 0.130 & 44,170 & 0.072 \\ 42,960 & S_8 & 45,555 & 0.020 & 46,911 & 0.399 & 45,249 & 0.021 \\ 41,494 & 40,820 & S_7 & 45,310 & 0.198 & 46,256 & 0.001 & 48,544 & 0.004 & 48,948 & 0.001 \\ 49,261 & 49,734 & S_{10} & 51,020 & 0.002 & 51,086 & 0.01 & 48,544 & 0.004 & 48,948 & 0.001 \\ 49,261 & 49,734 & S_{10} & 51,020 & 0.002 & 51,086 & 0.001 & 48,544 & 0.004 & 48,948 & 0.001 \\ 49,261 & 49,734 & S_{10} & 51,020 & 0.002 & 51,086 & 0.001 & 48,544 & 0.004 & 48,948 & 0.001 \\ 49,261 & 49,734 & S_{10} & 51,020 & 0.002 & 51,086 & 0.001 & 48,544 & 0.004 & 48,948 & 0.001 \\ 49$			36,343	$S_4$	36,437	0.001	36,907	0.001	34,928	0.001	35,386	0.001	
$ \begin{array}{c} 42,553 \\ 41,655 \\ 41,655 \\ 57 \\ 45,570 \\ 45,740 \\ 59 \\ 57 \\ 45,740 \\ 59 \\ 51,102 \\ 51$			38,416	S <sub>5</sub>	40,464	0.023	40,888	0.047	38,283	0.023	39,324	0.045	
$ \begin{array}{c} 41,655 \\ 43,682 \\ 43,682 \\ 58 \\ 45,740 \\ 58 \\ 51,102 \\ 51,102 \\ 51,102 \\ 51,102 \\ 51,29 \\ 51,102 \\ 51,29 \\ 51,102 \\ 51,29 \\ 51,102 \\ 51,29 \\ 51,102 \\ 51,29 \\ $		42,553	41,137	S <sub>6</sub>	42,007	0.022	42,110	0.033	40,230	0.014	39,818	0.026	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			41,655	S <sub>7</sub>	45,570	0.210	46,432	0.021	43,998	0.122	44,944	0.006	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			43,682	S <sub>8</sub>	46,773	0.178	46,773	0.178	44,181	0.213	45,086	0.035	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			45,740	S <sub>9</sub>	47,664	0.265	47,664	0.264	45,122	0.045	45,829	0.393	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $			51,102	S <sub>10</sub>	51,229	0.002	51,229	0.002	48,787	0.001	49,044	0.000	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Ethanol	27.322	25.912	S <sub>1</sub>	25,114	0.027	23.452	0.024	22,988	0.020	21.413	0.018	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		- )-	28.009	S <sub>2</sub>	31.874	0.006	31.967	0.008	30,581	0.005	30,487	0.006	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			30.872	S <sub>3</sub>	33.852	0.005	33.714	0.005	32.051	0.006	31.847	0.007	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			34.119	S <sub>4</sub>	36.649	0.001	37,160	0.001	35.211	0.001	35.714	0.000	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		41,493	35.183	S <sub>5</sub>	39.023	0.021	39,745	0.049	36,765	0.017	38.023	0.038	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		,	36,911	S <sub>6</sub>	41,156	0.017	40,666	0.022	39,370	0.016	38,610	0.025	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		49,505	40.716	S7	44,926	0.087	45,785	0.034	42,735	0.130	43.668	0.086	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			42,338	S <sub>8</sub>	45,106	0.311	46,533	0.432	43,859	0.247	45,249	0.194	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			43.334	So	46.926	0.008	46.838	0.016	45.662	0.010	45,455	0.175	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			50,119	S <sub>10</sub>	51,046	0.002	51,203	0.000	48,780	0.004	49,261	0.001	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Acetonitrile	27.248	26.211	S <sub>1</sub>	25,920	0.028	24.366	0.025	23,809	0.021	22,292	0.019	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1 iootomuno	_,,	28,981	S <sub>2</sub>	31,656	0.006	31,817	0.008	30,395	0.005	30,404	0.007	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			34 273	S2	33,900	0.004	33,781	0.003	32,154	0.005	31,898	0.005	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			36.520	S₄	36,500	0.001	38,982	0.001	35.087	0.001	35.537	0.000	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			37.740	S-5	39,662	0.023	40.243	0.049	37,453	0.020	38,580	0.046	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			39.075	S <sub>6</sub>	41.533	0.018	41.235	0.027	39.682	0.015	38,986	0.021	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		41,494	40.820	S <sub>7</sub>	45.310	0.198	46.266	0.071	43,290	0.130	44,170	0.072	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		, -	42.960	S <sub>8</sub>	45,454	0.185	46,555	0.003	44.052	0.232	45.004	0.012	
49,261 49,734 S <sub>10</sub> 51,020 0.002 51,086 0.001 48,544 0.004 48,948 0.001			46.087	So	46.555	0.020	46.911	0.399	45.249	0.022	45.517	0.363	
tig tig		49,261	49.734	S <sub>10</sub>	51.020	0.002	51.086	0.001	48,544	0.004	48,948	0.001	
			Ť.						Ř	e .			
syn form			svn form						anti forn	6 1			

with nitro group in *ortho-* and *meta* position corresponds to the  ${}^{1}L_{b}$  transition. In the spectra of M3M5NP the band  ${}^{1}L_{b}$  is overlapped by an intense and the most red-shifted band  ${}^{1}L_{a}$ , as in the *para* nitroaniline [37] and 2-amino-5-nitropyridine [13,14]. The bands in region ~ 50,000 cm<sup>-1</sup> correspond to the excitation of the substituents.

The all studied compounds include three substituents: (1) the nitro group (strong electron acceptor), (2) the methylamino group (strong electron donor) and (3) the methyl group which interact by hyperconjugation and steric effects. Only the methylamino group is always in the 2-position of the pyridine ring. The nitro and methyl groups change the position in the pyridine ring. The interactions between these substituents also change due to steric hinderance, intra- and intermolecular hydrogen bonding or a different contribution of the resonance forms.

The  ${}^{1}L_{b}$  band of M5M4NP exhibit the red shift from 27,000 to 25,500 cm<sup>-1</sup> and larger intensities than that in

Comparison of the calculated and experimental excitation energies  $(cm^{-1})$  and oscillator strengths for 2-(*N*-methylamino)-5-methyl-4-nitropyridine in Nujol mull and *n*-heptane, ethanol and acetonitrile solution

Solvent	Exp.	Gaussian	Singlet	Calculate	d excitation	energies						
		deconvolution	state	MPW1PV	W91/6-31G(	d.p)		B3LYP/	6-31G(d.p)			
				syn form		anti form	l	syn form		anti form		
Nujol	25,773	25,658	<b>S</b> <sub>1</sub>	24,594	0.036	24,707	0.031	24,432	0.036	23,027	0.025	
-		27,910	$S_2$	30,950	0.000	31,084	0.001	29,387	0.000	29,775	0.001	
		30,670	<b>S</b> <sub>3</sub>	34,025	0.001	33,774	0.001	32,289	0.001	32,069	0.000	
		33,882	$S_4$	35,868	0.001	35,871	0.001	34,855	0.000	34,483	0.000	
		37,979	$S_5$	41,632	0.007	41,330	0.020	41,254	0.011	39,791	0.013	
	42,017	41,718	S <sub>6</sub>	42,626	0.034	43,444	0.037	41,911	0.004	41,249	0.022	
		43,221	S <sub>7</sub>	45,725	0.127	45,335	0.107	45,025	0.114	43,299	0.130	
		44,278	S <sub>8</sub>	47,461	0.505	47,170	0.342	46,512	0.563	45,779	0.134	
		45,885	So	48,567	0.001	47,778	0.209	47,528	0.000	46,098	0.378	
		50,286	S <sub>10</sub>	50,454	0.123	50,659	0.104	48,996	0.115	48,897	0.095	
<i>n</i> -heptane	26,596	25.685	S <sub>1</sub>	23,764	0.034	23,908	0.030	23.641	0.034	22,198	0.024	
n' neptune	20,070	27,716	S <sub>2</sub>	31,107	0.000	31,230	0.001	29,551	0.000	29,896	0.001	
		29 328	S <sub>2</sub>	33,857	0.001	33,536	0.001	32 072	0.001	31,780	0.000	
		34 452	S.	35 951	0.001	35,972	0.000	35,026	0.000	34 627	0.000	
		37 191	54 S-	41 100	0.009	40,869	0.019	40.617	0.009	39 317	0.013	
		38,800	S	42.061	0.025	42 914	0.027	41 459	0.005	40 664	0.015	
	42 553	42 043	S-	45 153	0.023	44 748	0.122	44 603	0.000	42 753	0.143	
	42,555	44 340	S <sub>o</sub>	47,133	0.134	47,740	0.122	46 296	0.583	42,733	0.145	
		46 280	58 S-	48,638	0.001	47,170	0.977	40,200	0.000	46,002	0.229	
		40,200	59 S	50 801	0.110	50,650	0.004	40.383	0.000	40,002	0.085	
Ethernel	25 575	49,750	510 C	21 (01	0.110	21,807	0.095	49,385	0.100	49,585	0.000	
Ethanol	25,575	25,852	$S_1$	21,691	0.029	21,897	0.020	21,054	0.029	20,089	0.020	
		26,048	$S_2$	31,462	0.000	31,525	0.001	29,940	0.000	30,029	0.001	
		30,323	S3	33,380	0.001	35,218	0.001	31,720	0.001	31,509	0.000	
		37,291	$S_4$	36,343	0.000	36,400	0.000	35,574	0.000	35,106	0.000	
	41 40 4	40,427	S <sub>5</sub>	39,676	0.013	39,648	0.015	39,032	0.006	38,008	0.010	
	41,494	40,509	S <sub>6</sub>	40,734	0.010	41,630	0.007	40,306	0.012	39,280	0.006	
		41,363	S <sub>7</sub>	43,851	0.152	43,423	0.153	43,611	0.127	41,489	0.166	
		42,804	S <sub>8</sub>	46,707	0.549	46,533	0.573	45,767	0.603	45,358	0.528	
		46,331	S <sub>9</sub>	49,043	0.001	47,778	0.009	48,193	0.001	46,290	0.012	
		50,307	$S_{10}$	51,894	0.097	52,138	0.087	50,251	0.089	50,525	0.078	
Acetonitrile	25,445	24,855	$S_1$	22,525	0.031	22,712	0.027	22,452	0.030	20,952	0.022	
		27,516	$S_2$	31,315	0.000	31,407	0.001	29,815	0.000	29,984	0.001	
		30,276	$S_3$	33,560	0.001	33,245	0.001	31,706	0.001	31,492	0.000	
		36,129	$S_4$	36,140	0.000	36,192	0.000	35,311	0.000	34,884	0.000	
		37,989	$S_5$	40,290	0.013	40,160	0.017	39,667	0.007	38,567	0.012	
	41,667	40,597	S <sub>6</sub>	41,222	0.015	42,123	0.014	40,750	0.009	39,814	0.008	
		42,046	$S_7$	44,358	0.147	43,937	0.142	43,995	0.124	41,992	0.159	
		44,259	$S_8$	46,926	0.541	46,729	0.002	45,997	0.597	45,527	0.487	
		46,135	$S_9$	48,709	0.001	47,506	0.024	47,801	0.000	46,019	0.047	
		48,858	$S_{10}$	51,520	0.100	51,760	0.088	49,950	0.090	50,078	0.079	
		the.						À	C			
		syn form						anti form	L			

the case of M3M4NP (see Tables 1 and 2). The reason of such behaviour is the steric *ortho* effect.

The literature data on the methylated pyridine N-oxide derivatives [38] show that the conjugation of the nitro group with pyridine ring is sterically hindered in compounds where the methyl group is adjacent to the nitro group (*ortho* effect). This is the case of M3M4NP, M5M4NP and M5M3NP. Thus, the differences between the patterns of absorption spectra of the isomers are related to a different

substitution position of the methyl group and its influence on their structural and spectroscopic properties.

It is possible that steric hindrance between the nitro and methyl or methylamino substituents forces the nitro group to wag or twist against the pyridine ring in the studied compounds. The calculation of the structure of these compounds in the  $S_0$  state was performed with the molecular orbital calculations (GAUSSIAN 98W, MPW1PW91/6-31G(d,p) and B3LYP/6-31G(d,p)). The results of the

Comparison of the calculated and experimental excitation energies  $(cm^{-1})$  and oscillator strengths for 2-(*N*-methylamino)-3-methyl-5-nitropyridine in Nujol mull and *n*-heptane, ethanol and acetonitrile solutio

Solvent	Exp.	Gaussian	Singlet	Calculated excitation energies								
		deconvo-	state	MPW1PV	V91/6-31G(d	.p)		B3LYP /6				
		lution		syn form		anti form		syn form		anti form		
Nujol		22,462	S <sub>1</sub>	32,187	0.006	32,338	0.000	30,769	0.008	30,921	0.000	
	23,365	23,136	$S_2$	33,141	0.348	33,436	0.352	31,646	0.318	31,918	0.325	
	24,938	24,588	S <sub>3</sub>	34,827	0.002	34,592	0.001	33,289	0.002	33,422	0.001	
		28,745	$S_4$	38,262	0.023	38,610	0.037	37,244	0.019	37,636	0.031	
	32,573	33,352	S <sub>5</sub>	39,671	0.000	39,680	0.000	37,821	0.001	37,876	0.000	
		37,789	S <sub>6</sub>	43,517	0.004	43,588	0.003	42,105	0.075	42,499	0.004	
	39,682	40,010	$S_7$	44,285	0.086	45,108	0.100	42,517	0.009	42,937	0.094	
	43,859	43,758	S <sub>8</sub>	49,900	0.035	50,607	0.000	47,534	0.001	47,574	0.000	
		46,006	S <sub>9</sub>	50,582	0.001	51,229	0.037	84,216	0.052	49,383	0.035	
	51,282	51,395	S <sub>10</sub>	51,046	0.074	51,573	0.108	49,020	0.051	49,702	0.094	
<i>n</i> -heptane	29.240	28,779	$S_1$	32.362	0.268	32.644	0.265	30.817	0.270	31.133	0.314	
1	30,488	30,779	$S_2$	32,679	0.087	32,688	0.085	31,191	0.057	31,269	0.009	
		33,790	$\tilde{S_3}$	34,602	0.001	34,916	0.000	33,245	0.001	33,311	0.000	
		35,288	$S_4$	38,022	0.023	38,417	0.037	36,969	0.018	37,439	0.030	
		37,181	$S_5$	39,499	0.001	39,479	0.000	37,693	0.001	37,722	0.000	
		40,247	S <sub>6</sub>	43,485	0.071	43,744	0.003	41,356	0.083	42,123	0.100	
	45,454	42,828	S <sub>7</sub>	43,719	0.022	44,326	0.105	42,662	0.004	42,680	0.004	
		44,951	$S_8$	49,751	0.044	50,519	0.062	47,870	0.064	48,757	0.000	
		47,046	So	51,282	0.008	51,813	0.000	48,638	0.000	48,948	0.057	
	50,000	50,444	S <sub>10</sub>	51,813	0.007	52,110	0.091	49,020	0.003	50,226	0.003	
Ethanol	27.548	26,957	S.	30,581	0.354	30,766	0.344	29.078	0.325	29,260	0.319	
Lunanoi	21,010	29.057	S <sub>2</sub>	33,422	0.001	33,542	0.000	32,020	0.001	32,144	0.000	
	33,333sh	32.088	$S_2$	34.831	0.000	34,792	0.000	33,080	0.000	33,047	0.000	
	00,0000	34.275	S,	37.243	0.023	37,801	0.037	36,219	0.016	36,792	0.026	
		39,226	S5	39,448	0.002	39,463	0.000	37,764	0.002	37,836	0.000	
		41.065	S <sub>c</sub>	41.736	0.094	42.484	0.121	39,557	0.091	40.274	0.120	
		42.738	~0 S7	44.267	0.004	44 444	0.003	43,290	0.004	43 422	0.003	
	44.444	44.809	S.	48.591	0.064	49.456	0.046	46.296	0.067	47.103	0.047	
	,	47.661	So	49,480	0.009	50,736	0.052	47.916	0.022	49.285	0.063	
	49.751	50.094	S10	53,107	0.071	53.419	0.072	51.282	0.002	51,493	0.000	
Aceto-	27 248	26 721	S.	31 242	0.352	31 429	0.346	29 771	0.324	29.931	0.320	
nitrile	27,240	28,721	S <sub>1</sub>	33.051	0.002	33 195	0.000	31 625	0.002	31 796	0.000	
mune		31 464	S <sub>2</sub>	34 742	0.000	34 737	0.000	33,058	0.000	33 025	0.000	
	33,333sh	34.024	S,	37,555	0.022	38,050	0.036	36,536	0.017	37,051	0.027	
	00,0000	37 494	S <sub>4</sub>	39 336	0.001	39 340	0.000	37,622	0.001	37 679	0.000	
		40.031	S <sub>c</sub>	42 363	0.092	43 079	0.115	40,225	0.089	40 883	0.113	
		41 915	S <sub>7</sub>	43 888	0.005	44 033	0.003	42 918	0.004	42 992	0.003	
	45 045	44 510	S <sub>e</sub>	49.068	0.058	50,100	0.055	47 037	0.069	47 824	0.049	
	15,015	46.901	So	50.075	0.008	51,151	0.037	48.262	0.013	49,579	0.054	
	49 504	49 761	Sto	52 604	0.073	52 966	0.073	50,251	0.001	50 531	0.000	
	.,		k ≪	- ,		- ,		-	k			
		syn form						anti torm	1			

calculations show that nitro group and pyridine ring are in a twisted position. The dihedral angles between the pyridine ring and the nitro group are about -24 and  $-27^{\circ}$  (B3LYP) as well as 29 and 33° (MPW1PW91) for M3M4NP *anti* and *syn* form, respectively. In the M5M4NP *anti* and *syn* form those dihedral angles are -6 and 8° (B3LYP) and  $\sim 0^{\circ}$  (MPW1PW91), respectively. Steric hinderance, as a result of twisting of nitro group in respect to pyridine ring, may cause a decrease of CT band intensity and a slight change in

the transition energy, as it is observed in the spectra of M5M4NP and M3M4NP. The substitution of the methyl group in *para* position to methylamino group causes the red shift and the intensity of CT band increase. In this case the conjugated system of this molecule is significantly larger than in M3M4NP. The bathochromic shift of the CT band of the M5M4NP in respect to M3M4NP isomer (25,773  $\rightarrow$  27,100, 26,596  $\rightarrow$  28,409, 25,575  $\rightarrow$  27,322, and 25,445  $\rightarrow$  27,248 cm<sup>-1</sup>) is observed for the spectra in Nujol mull,

Comparison of the calculated and experimental excitation energies  $(cm^{-1})$  and oscillator strengths for 2-(*N*-methylamino)-5-methyl-3-nitropyridine in Nujol mull and *n*-heptane, ethanol and acetonitrile solution

Solvent	Exp.	Gaussian deconvolution	Singlet	Calculated excitation energies								
			state	MPW1PV	W91/6-31G(	d.p)		B3LYP /	6-31G(d.p)			
				syn form		anti form	l	syn form		anti form		
Nujol	23,923	22,831	S <sub>1</sub>	28,874	0.085	27,726	0.133	27,495	0.083	26,567	0.125	
		23,963	$S_2$	32,368	0.003	31,860	0.000	30,497	0.001	30,386	0.000	
	29,762	25,603	$S_3$	35,325	0.004	33,985	0.000	33,636	0.004	32,478	0.000	
	37,313	31,696	$S_4$	39,119	0.018	37,959	0.001	37,313	0.004	36,443	0.000	
		36,165	$S_5$	39,921	0.035	41,755	0.042	38,790	0.039	40,355	0.026	
	43,860	37,333	S <sub>6</sub>	45,099	0.046	43,967	0.056	43,048	0.074	42,052	0.065	
		43,546	$S_7$	46,292	0.031	46,292	0.008	44,763	0.017	44,405	0.005	
		44,946	S <sub>8</sub>	47,059	0.104	47,733	0.002	45,228	0.001	46,296	0.002	
		45,612	$S_9$	48,638	0.394	48,780	0.443	47,059	0.376	47,348	0.309	
		51,444	S <sub>10</sub>	50,176	0.017	50,454	0.195	47,755	0.092	48,426	0.290	
<i>n</i> -heptane	24,213	23,939	$S_1$	28,476	0.086	27,421	0.135	27,086	0.084	26,268	0.126	
1	,	25,937	$S_2$	32,541	0.002	32,030	0.000	30,722	0.001	30,545	0.000	
		32,514	S <sub>3</sub>	35,358	0.004	33,894	0.000	33,625	0.004	32,369	0.000	
		36,528	$S_4$	39,025	0.019	38,086	0.000	37,299	0.003	36,591	0.000	
	37.175	38,584	S-5	39,781	0.028	41.608	0.037	38,610	0.035	40,194	0.023	
	,	41.250	S <sub>6</sub>	44,786	0.050	43.649	0.060	42,698	0.079	41.739	0.070	
	44,053	43,351	S <sub>7</sub>	46,262	0.051	45,952	0.006	44,484	0.008	44,033	0.006	
	,	44,777	S <sub>8</sub>	46,860	0.044	47.755	0.002	45,228	0.005	46.313	0.002	
		47.129	So	48,379	0.434	48,709	0.469	46,948	0.419	47.370	0.378	
		49.719	S10	50,607	0.026	50.813	0.174	48,239	0.073	48,773	0.223	
Ethanol	23.585	23.126	S.	27.311	0.089	26.694	0.0139	25.947	0.086	25.549	0.130	
Buildinoi	20,000	24 766	S <sub>2</sub>	33,136	0.001	32 496	0.000	31 407	0.001	30,960	0.000	
		29.168	S <sub>2</sub>	35,401	0.005	33,898	0.000	33,523	0.005	32,383	0.000	
	37.037	36,406	S,	38,716	0.027	38,586	0.000	37,481	0.004	37,133	0.000	
	57,007	39 732	S <sub>5</sub>	39,610	0.011	41 186	0.028	38.081	0.024	39,698	0.014	
	43,860	41,510	Sc	43,888	0.061	42.918	0.066	41,754	0.090	41.068	0.078	
	.2,000	43.375	S <sub>7</sub>	45,435	0.023	44,980	0.014	43,178	0.001	43.029	0.015	
		45.023	S <sub>e</sub>	46,707	0.024	48.077	0.002	45,454	0.027	46.642	0.020	
		47 300	So	47 870	0.492	48 638	0.502	46 751	0.449	47 393	0.450	
		51,105	S10	51,706	0.037	51,773	0.144	49,480	0.065	49.726	0.151	
Acetonitrile	23 310	23.051	S 10	27.841	0.088	26.086	0.137	26.448	0.085	26.268	0.126	
Accontinuite	25,510	25,051	S.	32 838	0.000	20,980	0.137	20,448	0.005	20,208	0.120	
		23,127	52 S.	35 335	0.002	33 700	0.000	33 501	0.001	32 360	0.000	
	37 153	36 577	53 S	38 880	0.003	38 3 77	0.000	37 341	0.003	36 501	0.000	
	57,455	30,377	54 S	30,610	0.022	41 380	0.000	38 344	0.003	40 104	0.000	
	12 860	40.026	35 S	42 272	0.019	41,380	0.051	30,344 42 122	0.029	40,194	0.022	
	43,800	40,930	36 S	42,273	0.038	45,194	0.000	42,123	0.087	41,739	0.070	
		45,525	37 S	45,928	0.047	43,400	0.008	45,802	0.001	44,033	0.000	
		45,057	58 S	40,020	0.002	47,802	0.002	45,249	0.014	40,515	0.002	
		40,042	39 5	46,034	0.462	48,002	0.492	40,810	0.440	47,570	0.578	
		48,208	$S_{10}$	51,256	0.033	51,361	0.154	48,972	0.066	48,773	0.223	
		XG.						XX	<b>1</b> 0			
		syn form						<i>anti</i> form	h-1			

*n*-heptane, ethanol and acetonitrile solution, respectively. However, the position of  ${}^{1}L_{a}$  band is nearly unchanged (42,017, 42,553, 41,494, 41,667–41,494 cm<sup>-1</sup>). Wagging or twisting of substituent makes the resonance with the ring significantly weaker.

The optimised geometries of M5M3NP and M3M5NP show, that nitro group in M5M3NP is in a wagged and twisted position in the *syn* form, and the dihedral angles are about  $155^{\circ}$  (B3LYP) and  $157^{\circ}$  (MPW1PW91). However, in

anti form of M5M3NP and anti and syn forms of M3M5NP nitro group and pyridine ring are almost in the same plane. For anti form of M5M3NP and for anti and syn forms of M3M5NP also the amino nitrogen atom lies almost in the pyridine ring plane. The dihedral angles between amino nitrogen atom and pyridine ring are -177 and  $-179^{\circ}$ (B3LYP) as well as -176 and  $-178^{\circ}$  (MPW1PW91) for syn and anti form, respectively. This fact suggests a significant conjugation between the amino and nitro group via pyridine



Fig. 1. The UV/VIS spectra of M3M4NP measured for the Nujol mull and for the *n*-heptane, ethanol and acetonitrile solutions.

ring. The substitution of a nitro group in the *para* position to alkylamino group causes the red shift from c.a. 27,500 to c.a.  $23,500 \text{ cm}^{-1}$  and the intensity of the band increases in respect to the M5M3NP isomer (Table 5).

The absorption spectra of 4-dimethylaminopyridine show a shoulder at lower wavenumber side of the band at about  $38,460 \text{ cm}^{-1}$  [15]. The Mishina et al. [15] assume that the shoulder is due to 4-dimethylaminopyridine protonated or hydrogen-bonded with the solvent molecule at the pyridine nitrogen or at the amino nitrogen. The shoulders in the spectra of 3-methyl- and 3,5-dimethyl-4dimethylaminopyridine are not clear because they are either overlapped by broad main bands or the methyl groups at 3and 5-positions of pyridine ring block the interaction between solvent molecules and the dimethylamino group of solute molecules.

The bathochromic shift of the CT band in M5M3NP  $(23,585 \text{ cm}^{-1})$  when compared with M3M5NP  $(27,548 \text{ cm}^{-1})$  may suggest that planar configuration causes the formation of a additional quasi-aromatic system with intramolecular hydrogen bonding [39]. Such chelate ring causes a quite large changes of the UV spectrum. A similar behaviour is observed for isomers with methyl group in 4 or



Fig. 2. The UV/VIS spectra of M5M4NP measured for the Nujol mull and for the n-heptane, ethanol and acetonitrile solutions.



Fig. 3. The UV/VIS spectra of M3M5NP measured for the Nujol mull and for the *n*-heptane, ethanol and acetonitrile solutions.

6 position [40,41]. In region of about 37,000 cm<sup>-1</sup> a distinct band appears in the spectrum of M5M3NP. This band, which shows the lowest intensity and blue shift in relation to  ${}^{1}L_{b}$  band, corresponds to excitation of the M5M3NP molecule with intramolecular hydrogen bonding. The slight shift of this band may be due to a competetive hydrogen bonding between the solute and ethanol molecules (hypsochromic shift) and the solvation effects in polar acetonitrile solution (bathochromic shift).

The band  ${}^{1}L_{a}$  in the spectrum of M5M3NP is bathochromic shifted in relation to the bands in the 4- or 5- nitro isomers.

It seems that not the dipole moment (which is the largest for acetonitrile and the smallest for *n*-hepane) but the proton donating ability of solvent molecules is responsible for the solvent dependence of  $\lambda_{max}$ . The electronic absorption spectra of 4-(N-dimethylamino)-pyridine, 3-methyl-4-(Ndimethylamino)-pyridine and 3,5-dimethyl-4-(N-dimethylamino)-pyridine measured in cyklohexane (non-polar), chloroform (medium polar) and acetonitrile (highly polar) solutions behave in a similar way [15].

In a case of 5-nitro derivative, the conjugated system of the molecule is significantly larger than that in the 3-nitro



Fig. 4. The UV/VIS spectra of M5M3NP measured for the Nujol mull and for the *n*-heptane, ethanol and acetonitrile solutions.

Experimental electronic absorption spectra of M3M4NP, M5M4NP, M3M5NP and M5M3NP in different solvents								
Compound	$v_{\rm max}$ in Nujol mull	$v_{max}/(\varepsilon_{max})$ in <i>n</i> -heptane	$v_{\rm max}/(\varepsilon_{\rm max})$ in ethanol	$v_{\rm max}/(\varepsilon_{\rm max})$ in acetonitrile				
M3M4NP			49,505/(13,553)	49,261/(11,795)				
	42,017	42,553/(15,682)	41,493/(17,786)	41,494/(21,344)				
	27,100	28,409/(1779)	27,322/(1607)	27,248/(1747)				
NGN (AND	10.017	10 550 ((10 50.6)	41 40 4// 41 07 4	11 ((7/2) 277)				

Table 5 Experimental electronic absorption spectra of M3M4NP, M5M4NP, M3M5NP and M5M3NP in different solvents

	42,017	42,555/(15,082)	41,493/(17,780)	41,494/(21,544)
	27,100	28,409/(1779)	27,322/(1607)	27,248/(1747)
M5M4NP	42,017	42,553/(19,736)	41,494/(41,864)	41,667/(23,377)
	25,773	26,596/(1867)	25,575/(2870)	25,445/(1714)
M3M5NP		50,000/(18,280)	49,751/(8309)	49,504/(9227)
	43,859	45,454/(24,378)	44,444/(9789)	45,045/12,097)
	39,682			
	32,537	30,488/(30,584)	33,333sh/(4075)	33,333sh/(3991)
	24,938	29,240/(32,467)	27,548/(16,256)	27,248/(19,166)
	23,365			
M5M3NP	43,860	44,053/(19,183)	43,860/(27,250)	43,860/(29,404)
	37,313	37,175/(3606)	37,037/(4779)	37,453/(5295)
	29,762			
	23,923	24,213/(5639)	23,585/(7875)	23,310/(8772)

The wavenumbers (in cm<sup>-1</sup>) and molar extinction coefficient are denoted ( $\varepsilon_{max}$ ).

ones. It is seen from the comparison of their CT band intensities and calculated oscillator strengths corresponding to the intramolecular charge transfer (ICT) for these derivatives (Tables 1–5). The bathochromic shift for this transition is seen when the spectra in solutions are compared. The reason of such behaviour is a better stabilization of the resonance form of molecule in its excited state in a polar solvent.

The conformational effect could be considered for the all compounds studied. The theoretical values of the energy levels differ significantly from the experimental values (up to  $1000-4000 \text{ cm}^{-1}$ ) for the S<sub>1</sub> transitions. The biggest differences between experimental and calculated values are observed for the M3M5NP in Nujol mull (Fig. 5), where the interactions between neighbouring molecules are the strongest. The comparison of the calculated and experimental values shows (Tables 1–4 and Fig. 5) that the best agreement is observed for M3M4NP and M5M3NP in *n*-heptane solution.

### 6. Conclusions

- For all studied nitro derivatives of 2-(*N*-methylamino)picolines, the batochromic shift of the first band at 24,200–29,240 cm<sup>-1</sup> on passing from non-polar to polar solvent was observed. The largest shift appears for M3M5NP (1992 cm<sup>-1</sup>), although it takes a significant values also for M5M4NP, M5M3NP and M3M4NP (1151, 903 and 1161 cm<sup>-1</sup>, respectively). The shifts in electronic absorption spectra result from the solute solvent interaction. The electronic transition energy increases with increasing solvent polarity.
- 2. The band  ${}^{1}L_{a}$  of the  $\pi \rightarrow \pi^{*}$  transition of the pyridine ring, which for M5M3NP appears in region at about 44,000 cm<sup>-1</sup>, is not sensitive upon change of solvent polarity. Only weak bathochromic shift is observed

 $(193 \text{ cm}^{-1})$  on passing from *n*-heptane to acetonitrile solution. The greatest dependence is observed for this band in the region at about 42,000 cm<sup>-1</sup> for the isomers with the nitro group in position 4.



- 3. The bands of the electronic absorption spectra of M3M5NP and M5M3NP appearing in the 30,490-33,330 and 37,040-37,450 cm<sup>-1</sup> region, respectively, show significant blue shift in polar solvent.
- 4. The observed disagreement between theoretical and experimental results may be due to such reasons as steric hindrance, intra- and inter-molecular hydrogen bonding or a different contribution of the resonance polar form in these compounds. Steric hindrance may bring a decrease of CT band intensity and a slight change in energy of the transitions, as it is observed for M3M4NP, M5M4NP and M5M3NP.
- 5. The big difference between the spectra of M3M5NP measured in Nujol mull and the spectra in solvents may result from intermolecular interactions between the adjacent molecules. The formation of the intermolecular hydrogen bond between the amino hydrogen atom and nitro-group could stabilize the structure of these pyridine derivatives in the solid state.
- 6. The  $\pi \rightarrow \pi^*$  bands in the spectra of the studied series undergo a bathochromic shift and the  $n \rightarrow \pi^*$  bands undergo a hypsochromic shift on passing from *n*-heptane to ethanol and acetonitrile solvent.
- 7. The calculations performed for singlet states showed that better agreement for the prediction of the solvent effect is achieved with the application of the B3LYP/6-31G(d,p) theoretical model in respect to the MPW1PW91/6-31G(d,p) one.
- 8. The correlation between the calculated and experimentally observed transition energies is satisfactory: for absorption spectra in Nujol mull  $R^2 = 0.898 - 0.974$ , in *n*-heptane solution  $R^2 = 0.944 - 0.985$ , in ethanol solution  $R^2 = 0.930 - 0.973$  and in acetonitrile solution  $R^2 = 0.934 - 0.977$ . The best correlation between the calculated and experimentally observed transition energies was obtained for the *syn* form of M5M3NP in *n*-heptane solution calculated in B3LYP/6-31G(d,p) approximation ( $R^2 = 0.985$ ) and the worst for *anti* form of M3M5NP in Nujol mull, calculated by the same method ( $R^2 = 0.898$ ).

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