# Intermolecular Interactions of Pyridine Analogues of Picric Acid with Some Pyridine Bases

# J. J. KOZIOŁ and A. NOWEK

Institute of Chemistry, Pedagogical University, PL-42200 Częstochowa

Received 24 November 1992

UV VIS spectrophotometric and quantum-mechanical study on the interaction of 3-hydroxy-2,6-dinitropyridine (3HDNP) and 3-hydroxy-2,4,6-trinitropyridine (3HTNP) with selected pyridine bases is presented. The stability constants for complex formation in aqueous solution have been determined. Comparisons were made with corresponding complexes of polynitrophenols. The nature of interactions has been verified with semiempirical (AM1 and modified INDO) quantum-mechanical methods. It has been found that the values of stability constants for complex formation for 3HDNP and 3HTNP with pyridine bases in water are of comparable magnitude to those of picric acid in benzene solution.

In the previous papers [1-4] we have studied the nature of intermolecular interactions of some pyridine analogues of picric acid (PA), i.e. 3,5-dinitro-1Hpyrid-2-one (2HDNP), 3,5-dinitro-1H-pyrid-4-one (4HDNP), 3-hydroxy-2,6-dinitropyridine (3HDNP), and 3-hydroxy-2,4,6-trinitropyridine (3HTNP) with pyridine bases systems. The term "pyridine analoques of picric acid" is derived from considering the aza atom in pyridine ring as an intermolecular substituent more or less equivalent to the nitro group in benzene system. This assumption has been verified by studying the intermolecular interactions of selected hydroxynitropyridines with some pyridine bases. It has been found that 3HDNP and 3HTNP form molecular complexes the most similar to those of their polynitrophenol counterparts. It seems to be important here that for 3HDNP and 3HTNP tautomeric keto forms do not exist, unlike for 2HDNP and 4HDNP. In the present paper the more adequate UV VIS spectrophotometric and quantum-mechanical studies on intermolecular interactions of 3HDNP and 3HTNP with selected pyridine bases are reported. Also, taking into account that  $pK_a$  values for 3HDNP and 3HTNP are close to those of some dinitrophenols. comparisons with corresponding 2,6-dinitrophenol (2,6-DNPh)-pyridine systems are made.

## EXPERIMENTAL

3-Hydroxy-2,4,6-trinitropyridine (3HTNP) was prepared according to the method described in [5] and was purified by crystallization from methanol (m.p. = 120-121 °C). All pyridines, three isomeric picolines, 2,3-, 2,4- and 2,6-lutidines and 2,4,6-collidine of anal. grade were commercially available. They were dried over solid sodium hydroxide and distilled prior to use. Water was twice distilled. All the stability constants were determined spectrometrically at (20 ± 0.1) °C in aqueous solution using a Specord UV VIS spectrometer (Zeiss, Jena) equipped with a  $10^{-2}$  m quartz cell and our own original thermostat (an electrical heating-jacket controlled with UNIPAN (Poland) temperature regulator). In measurements the pyridine bases concentration covers the range 0.1–0.6 mol dm<sup>-3</sup> and the concentrations  $10^{-4}$  mol dm<sup>-3</sup> for hydroxynitropyridines were kept constant throughout.

## **RESULTS AND DISCUSSION**

3-Hydroxypyridine in aqueous solution exists mainly in zwitterionic, as well as not dissociated forms with the presence of only small amount of ionic intermediates [6]. However, for its nitro derivatives the ionic forms dominate. For this reason, the interactions of 3HDNP and 3HTNP with selected pyridine bases in aqueous solution should be quite accurately described by the following equations

 $B + HA \rightleftharpoons B...HA$  (hydrogen bond) (A)

B...HA  $\rightleftharpoons$  BH<sup>+</sup>A<sup>-</sup> (ion pair) (B)

where B and HA denote pyridine and 3HDNP or 3HTNP, respectively.

We recognize that water is a very unconvenient solvent for the acid-base equilibria presented here, however, it is the only common one for all compounds under study. It has been found [3, 4] that UV VIS absorption spectra of not dissociated 3HDNP and 3HTNP are substantially different from their dissociated forms, *i.e.* longwave absorption bands in the visible region of spectra for corresponding anions are observed. In general, studies on intermolecular interactions considered here are performed with spectrophotometric or potentiometric methods. Frequently, use of the spectrophotometric techniques allows to determine molecular forms of interacting systems. Therefore, the quantum-chemical calculations of low-lying electronically excited states for various hypothetic forms of 3HDNP



followed by careful comparison of calculated data with the experimental ones seem to be a suitable way to determine the nature of intermolecular interaction and complex formation of these species. The above forms of 3HDNP and 3HTNP have been taken into account, as well as their phenol analogues, *i.e.* polynitrophenols with  $pK_a$  very close to those of hydroxypyridines studied here: picric acid (PA), 2,4-dinitrophenol (2,4-DNPh), 2,6-dinitrophenol

Table 1. Calculated and Experimental Torsion Angles for NO<sub>2</sub> Groups around C—N Bond for PA, 2,4-DNPh, and 2,6-DNPh and Their Anions

Compound	Position	<i>α</i> /°	
Compound	FUSILION	exp.	calc.
PA	2	4.3 <sup>a</sup> , 3.9 <sup>b</sup>	0.33
	4	11.4 <sup>a</sup> , 3.9 <sup>b</sup>	0.20
	6	27.1°, 50.9 <sup>b</sup>	6.17
PA <sup>−</sup>	2	41.2ª	11.20
	4	3.7ª	0.60
	6	29.4ª	1.33
2,4-DNPh	2	2.58°	0.14
	4	4.84 <sup>c</sup>	0.13
2,4-DNPh <sup>-</sup>	2	—	0.06
×	4	-	0.06
2,6-DNPh	2	13.10 <sup>d</sup>	6.40
	6	2.67 <sup>d</sup>	0.40
2,6-DNPh⁻	2	-	6.37
	6	-	1.00

a) Ref. [9]; b) Ref. [10]; c) Ref. [11]; d) Ref. [12].

(2,6-DNPh), and their anions. Excitation energies and the respective oscillator strengths are calculated with LCAO MO SCF modified INDO CI method [7] (the adjustable parameter for resonance integral was equal to 0.9 and 50 low-lying monoexcited singlet configurations in configuration interaction procedure were included). Because of lack of experimental geometrical data for selected hydroxypyridine systems we have performed geometry optimization with semiempirical AM1 method using AMPAC package [8] for all systems studied here. The nearly full geometry optimization with C1 symmetry was performed, i.e. planarity of aromatic ring atoms was imposed. It should be noted that for some of polynitrophenol systems crystallographic structures are known [9-12]. Therefore, the useful comparison of calculated and observed geometrical data is available. More significant discrepancies have been found for spatial orientation of nitro groups in polynitrophenols (Table 1). The calculated values of dihedral angle between nitro group and benzene ring plane are significantly smaller than the corresponding experimental ones. This general tendency as observed for polynitrophenols seems not to be so completely supported for pyridine analogues (Table 2). For 3HDNP<sup>-</sup> and 3HTNP<sup>-</sup> (Table 2), *i.e.* systems for which no intramolecular hydrogen bond exists AM1 calculations predict nearly perpendicular orientation for nitro group plane in position 2 in contrast to picric acid one (Table 1). It does not seem to be an AM1 method artifact, since nearly identical orientation with MNDO and MINDO/3 has been predicted. Optimal AM1 geometries were used for calculation of longwave electronic transitions for all of hypothetic systems studied here and the experimental data for acidic or basic aqueous solution of PA, 2,4-DNPh, 2,6-DNPh, 3HDNP, and 3HTNP were obtained by UV VIS measurements. The observed and corresponding calculated excitation energies and oscillator strengths for these systems are listed in Table 3. Appropriate changes of pH of aqueous solutions allow to obtain various forms of 3HDNP and 3HTNP. It should be noted that for 3HTNP the same longwave absorption band in 1,2-dichloroethane/pyridine base as for the aqueous solution at pH > 7 was observed [4]. Also, addition of pyridine bases to aqueous solution of 3HDNP does not cause any significant longwave shifting of the longwave

Table 2. Calculated Torsion Angles for NO<sub>2</sub> Groups around C—N Bond for 3HDNP and 3HTNP and Their Ionic Forms

3HDNP	3HDNP <sup>-</sup>	3HDNP <sup>-</sup> H <sup>+</sup>	<b>3HTNP</b>	3HTNP <sup>-</sup>	3HTNP <sup>-</sup> H <sup>+</sup>		
Position							
2	1.92	93.00	0.23	0.23	89.50	1.11	
4				2.00	1.31	0.21	
6	0.26	0.16	0.06	1.73	1.86	6.50	

Table 3.Calculated and Experimental Wavenumbers  $\tilde{v}$  Corresponding to Longwave Transition Energies  $\Delta E$  and Oscillator Strengths,<br/>f for Various Forms of PA, 2,4-DNPh, 2,6-DNPh, 3HDNP, and 3HTNP

0	$\widetilde{v}$	$f_{calc}$	$\widetilde{v}$	$f_{exp}$
Compound	cm <sup>-1</sup>	kN m <sup>−1</sup>	cm <sup>-1</sup>	kN m <sup>−1</sup>
PA	29 430	0.030	29 500	0.090
PA <sup>−</sup>	28 805	0.360	28 333	0.340
	23 786	0.202	24 333	0.170
2,4-DNPh	29 963	0.023	28 426	0.014
2,4-DNPh <sup>-</sup>	24 832	0.234	23 000	0.173
2,6-DNPh	29 460	0.059	28 249	0.101
2,6-DNPh <sup>−</sup>	29 367	0.005	27 333	0.274
	22 550	0.280	25 000	0.128
<b>3HDNP</b>	31 909	0.069	29 833	0.135
	28 855	0.070		
3HDNP <sup>-</sup>	26 905	0.005		
	26 802	0.324	25 000	0.562
	24 582	0.237		
3HDNP <sup>-</sup> H <sup>+</sup>	28 602	0.148		
	19 746	0.249		
<b>3HTNP</b>	31 735	0.030	29 833	0.069
	28 557	0.122		
3HTNP <sup>-</sup>	32 641	0.059	30 000	0.072
	27 973	0.398		
	25 870	0.017	25 000	0.072
	24 013	0.202		
3HTNP <sup>-</sup> H <sup>+</sup>	28 624	0.148		
	19 466	0.220		
	19 335	0.029		

Table 4. Stability Constants K for Molecular Complexes of 3HDNP and 3HTNP with Selected Pyridine Bases in Aqueous Solution

	pK <sub>a</sub> of base	K(3HDNP) · 104 a	K(3HTNP) · 10 <sup>4</sup> <sup>a</sup>	
Base		dm <sup>3</sup> mol <sup>-1</sup>	dm <sup>3</sup> mol <sup>-1</sup>	
Pyridine	5.17	1.07 ± 0.03	0.57 ± 0.02	
$\alpha$ -Picoline	5.97	0.87 ± 0.03	$0.90 \pm 0.03$	
$\beta$ -Picoline	5.68	$1.56 \pm 0.05$	0.15 ± 0.01	
γPicoline	6.02	$1.15 \pm 0.03$	$1.29 \pm 0.04$	
2,3-Lutidine	6.57	$0.59 \pm 0.02$	0.50 ± 0.01	
2,4-Lutidine	6.63	0.81 ± 0.02	$0.53 \pm 0.02$	
2,6-Lutidine	6.58	$1.03 \pm 0.03$	0.31 ± 0.01	
2,4,6-Collidine	7.58	1.01 ± 0.03	0.78 ± 0.02	

#### a) Ref. [3].

absorption band. The agreement between experimental transitions and the calculated ones is very good. The longwave absorption band at  $\tilde{v} = 25000$ 

 $\rm cm^{-1}$  of analytic importance for 3HTNP as well as 3HDNP—pyridine base systems has been found. From this observation and the analysis of data col-

Table 5. Stability Constants K for Molecular Complexes of Picric Acid (PA) and 2,6-DNPh with Selected Pyridine Bases as Measured in Various Solvents

	K · 10⁴/(dm³ mol <sup>-1</sup> ) .				
Base	PA in benze	2,6-DNPh ene [14]	2,6-DNPh in chloro- benzene [14]	PA in acetone [15]	PA in nitro- methane [16]
	$\varepsilon_{\tau} = 2$	2.272	$\varepsilon_r = 5.62$	$\varepsilon_r = 20.7$	$\varepsilon_{\rm r} = 35.8$
Pyridine	0.42	4.35	6.35	0.22	2.43
α-Picoline	2.08	3.57	6.03		5.10
$\beta$ -Picolińe	1.13				1.96
γ-Picoline	2.04			5.08	
2,4-Lutidine				9.9	
2,6-Lutidine	4.88				1.28
2,4,6-Collidine	11.10	111	159		9.23

lected in Table 3 it can be concluded that (i) ionic 3HTNP<sup>-</sup> and 3HDNP<sup>-</sup> forms are present and (ii) the other forms of 3HTNP and 3HDNP are excluded in complex system solution studied here. As it follows, 3HTNP and 3HDNP with pyridine bases in aqueous solution form molecular complexes of ion pair type as described with eqn (B). Taking into account the above statements, stability constants K of the complexes 3HTNP and 3HDNP with pyridine bases in aqueous solution were determined according to the method of Ketelaar et al. [13] (Table 4). It should be noted that values of stability constants for 3HTNP and 3HDNP complexes studied here are of the same order for corresponding bases, however, in general for 3HDNP they are twice as large as for 3HTNP ones. Undoubtedly, it follows from a very large difference of pKa; 3.20 vs. 6.40 for 3HDNP and 3HTNP, respectively.

As we have assumed above, 3HTNP and 3HDNP may be considered as respective polynitrophenol analogues. The stability constants values of picric acid and 2,6-DNPh complexes with appropriate pyridine bases taken from literature are listed in Table 5. It should be noted that the stability constants for PA complexes are by four orders larger than those for 2,6-DNPh ones. It is quite obvious, taking into account very significant difference of  $pK_a$  values for PA and 2,6-DNPh systems. Moreover, no significant influence of solvent relative permittivity on the stability constant values for 3HTNP and 3HDNP complex formation with corresponding pyridine bases measured in water are very

close to the picric acid ones in benzene (Tables 4 and 5). The above observations correspond nicely with recent studies of *Smagowski et al.* [15, 16]. They have found no significant differences of basicity of pyridine in water, acetone, and nitromethane solutions, as well.

### REFERENCES

- 1. Kozioł, J. and Tomasik, P., Bull. Acad. Pol. Sci., Ser. Sci. Chim. 25, 688 (1977).
- Kozioł, J. and Tomasik, P., Bull. Acad. Pol. Sci., Ser. Sci. Chim. 27, 335 (1979).
- Kozioł, J., Nowek, A., and Tomasik, P., Gazz. Chim. Ital. 120, 403 (1990).
- 4. Kozioł, J. J., Gazz. Chim. Ital. 122, 143 (1992).
- 5. Czuba, W. and Płażek, E., *Rec. Trav. Chim. Pays-Bas* 77, 92 (1958).
- 6. Tieckelmann, H., in *Pyridine and its Derivatives*, Suppl. Part III, p. 740. Wiley, New York, 1974.
- Lipiński, J., Nowek, A., and Chojnacki, H., Acta Phys. Pol. A 53, 229 (1978).
- Mrozek, J. and Chłobowski, A., AMPAC-PC v. 1 a modified version of QCPE 505 program for IBM-PC.
- 9. Jensen, B., Acta Chem. Scand., B 29, 891 (1975).
- Herbstein, H. F. and Kaftory, M., *Acta Crystallogr.*, *B* 32, 387 (1976).
- 11. Iwasaki, F. and Kawano, Y., Acta Crystallogr., B 33, 2455 (1977).
- 12. Iwasaki, F., Sato, M., and Aiharo, A., *Acta Crystallogr., B 32,* 102 (1976).
- Ketelaar, J. A. A., van de Stolpe, C., Goudsmit, A., and Dzcubas, W., Rec. Trav. Chim. Pays-Bas 71, 1104 (1952).
- 14. Jasiński, T., Misiak, T., and Skarżyńska-Klentak, T., *Rocz. Chem. 42*, 875 (1968).
- 15. Smagowski, H. and Bartnicka, H., Pol. J. Chem. 62, 825 (1988).
- 16. Smagowski, H., Pol. J. Chem. 63, 215 (1989).