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# Spectroscopic and Theoretical Investigation of Molecular Complexes of 2,4,6-Trinitropyridine-1-oxide with Some Pyridine Derivatives

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**Summary.** Stability constants and enthalpies of formation were determined for *EDA* complexes of 2,4,6-trinitropyridine-1-oxide (*TNPO*) with some pyridine bases. Energies of transition, $h\nu_{CT}$, calculated by the SCF MO CI-1 PPP method fit well the corresponding experimental data. Based on these results, geometries for the systems under study are proposed.

**Keywords.** Molecular complexes; UV-VIS spectra, SCF MO CI-1 PPP.

### Spektroskopische und theoretische Untersuchung von molekularen Komplexen des 2,4,6-Trinitropyridin-1-oxids mit einigen Pyridinderivaten

**Zusammenfassung.** Es wurden Stabilitätskonstanten und Bildungsenthalpiewerte einiger *EDA*-Komplexe von 2,4,6-Trinitropyridin-1-oxid mit ausgewählten Pyridinbasen bestimmt. Dabei wurde eine gute Übereinstimnmung zwischen den Anregungsenergien $h\nu_{CT}$ aus den UV-VIS-Spektren und den mit der SCF-MO-CI-1 PPP-Methode errechneten Werten gefunden. Es werden für die untersuchten Komplexe entsprechende Strukturen vorgeschlagen.

## Introduction

In our recent papers [1–4] results of studies on molecular complexes of pyridine analogues of picric acid, trinitroanisole and trinitrobenzene with pyridine bases were presented. Various physiochemical investigations point to the $N^+ - O^-$ group of amine oxides to be an electron accepting moity [5] of the strength reflected by following Hammett constants ($\sigma_{\alpha,N^+-O^-} = 0.65$, $\sigma_{\beta,N^+-O^-} = 1.20$, $\sigma_{\gamma,N^+-O^-} = 1.53$ [5d]. One may assume that 2,4,6-trinitropyridine-1-oxide (*TNPO*) is a pyridine analogue of trinitrobenzene (*TNB*).

In the UV VIS absorption spectra of investigated systems composed of 2,4,6-trinitropyridine-1-oxide with one of pyridine, α-, β- and γ-picoline, 2,3-litudine, 2,6-lutidine and 2,4,6-collidine charge transfer (CT) bands are observed.

This speaks for the formation of electron-donor-acceptor (*EDA*) complexes. The recognition of some properties of these complexes and the function of 2,4,6-trinitropyridine-1-oxide as the acceptor in these complexes is the matter of this report.

## Experimental

2,4,6-Trinitropyridine-1-oxide was prepared according to [6]. Pyridine and its methyl derivatives (Fluka AG) were dried over KOH followed by distillation. The spectra in 1,2-dichloroethane were recorded using the Carl Zeiss Jena Specord UV VIS apparatus with a stabilization of temperature in the range ±0.1 K.

The concentrations of ethylene chloride solutions were $10^{-3}\,M$ for *TNPO* and 0.10, 0.20, 0.30, 0.40, 0.45, 0.50, 0.55, 0.60 $M$ for pyridine bases. The oscillator strength, $f$, of the *CT* bands were calculated from the relation [7]

$$f = 4.5976 \cdot 10^{-9} \cdot \varepsilon \cdot \Delta\nu_{1/2},$$

where $\varepsilon$ is the molar extinction coefficient in $dm^3\,mol^{-1}\,cm^{-1}$ and $\Delta\nu_{1/2}$ is the half width of the band in $cm^{-1}$.

The stability constants, $K$, of the complexes under study were determined according to Benesi and Hildebrand [8] and the enthalpy of formation, $\Delta H_f$, was derived from the van't Hoff isobar. We used the SCF MO CI-1 PPP method with mixing of monoexcited configurations. There were taken under consideration 49 configurations of lowest terms. The scheme of the parametrization was adopted from the report by Ohta et al. [9] with own modifications of relevant magnitudes (Table 1).

**Table 1.** Empirical parameters applied in the PPP CI-1 calculations

| | $I_D$ [eV] | $\gamma_{DD}$ [eV] | $D_D$ [eV] | $\zeta_D$ | $Z_D$ |
|---|---|---|---|---|---|
| $C^+$ | 11.16 | 11.13 | 12.50 | 1.625 | 1 |
| $C^+ (C \equiv N)$ | 12.69 | 10.90 | 14.50 | 1.625 | 1 |
| $N^+ (C \equiv N)$ | 16.18 | 11.52 | 20.00 | 1.95 | 1 |
| $C(-CH_3)$ | 10.15 | 11.13 | 14.50 | 1.625 | 1 |

**Table 2.** The spectral and thermodynamic characteristics of molecular complexes of *TNPO*

| Donor | $E_{exp.}$ [eV] | $f_{exp.}$ | $E_{calc.}$ [eV] | $f_{calc.}$ | $\theta$ [°] | $K^a$ [$dm^3\,mol^{-1}$] | $-\Delta H_f$ [$kcal\,mol^{-1}$] |
|---|---|---|---|---|---|---|---|
| Pyridine | 2.37 | 0.1113 | 2.95 | 0.2220 | 120 | 9.88±0.14 | 4.00±0.02 |
| α-Picoline | 2.79 | 0.0745 | 2.81 | 0.1963 | 120 | 19.87±0.42 | 2.48±0.01 |
| | 2.33 | | 2.14 | 0.0941 | 0 | | |
| β-Picoline | 3.47 | | 3.53 | 0.1036 | 240 | | |
| | 2.75 | 0.0671 | 2.87 | 0.0345 | 240 | 23.39±0.51 | 1.38±0.03 |
| γ-Picoline | 2.73 | 0.1470 | 2.76 | 0.1447 | 120 | 25.60±0.64 | 3.35±0.08 |
| | 2.23 | 0.1639 | 2.43 | 0.0348 | 120 | 2.08±0.05 | 0.21±0.01 |
| | 1.82 | 0.0675 | 1.67 | 0.3830 | 120 | 0.87±0.02 | 3.10±0.01 |
| 2,3-Lutidine | 2.79 | 0.0507 | 2.81 | 0.1947 | 240 | 2.34±0.09 | 5.78±0.01 |
| 2,6-Lutidine | 3.47 | | 3.59 | 0.4904 | 120 | | |
| | 2.85 | 0.0476 | 2.81 | 0.1979 | 120 | 1.98±0.05 | 0.37±0.01 |
| 2,4,6-Collidine | 3.78 | 0.1485 | 3.79 | 0.3761 | 120 | 20.81±0.55 | 0.71±0.02 |
| | 2.83 | 0.0274 | 2.87 | 0.0122 | 120 | 22.02±0.59 | 0.09±0.02 |

[a] Measurements at 298±0.1 K

## Results and Discussion

The formation of *EDA* complexes in mixed solutions can be recognized by comparisons of the UV VIS spectra of the solutions of individual compounds (*TNPO* and pyridine bases) and the mixture. For a majority of complexes more than one *CT* band is observed. Based on this observation, stability constants of these complexes and enthalpies of formation could be determined. They are presented in Table 2.

They are typical for *EDA* complexes of the b π → a π type. It may be accepted that the strength of the complex is described by its stability constant. From the comparison of the stability constants of relevant complexes of *TNPO* and *TNB* one may conclude that the stability constants for complexes with the first acceptor are higher by one order (Table 3).

The existence of more than one *CT* band in the spectra of investigated *EDA* complexes seems to deal with the structure of these complexes. This is proved by the SCF MO CI-1 PPP calculations for the systems studied. First the sandwich structure of these complexes was accepted arbitrarily with the 3.3 Å donor-acceptor inter-plane distance, since *CT* interaction energy is much more sensitive to donor-acceptor orientation than to intermolecular distance over the range 3.2–3.5 Å [10]. Standard bond lengths were taken between atoms in both donor and acceptor. Molecules of donor and acceptor were set in respect to one another in order to have their centres of aromatic ring overlapped. The θ angle between axes bisecting N 1 and C 4 atoms in both rings was a variable parameter (Fig. 1).

**Table 3.** Stability constants for complexes of trinitrobenzene (*TNB*) and 2,4,6-trinitropyridine-1-oxide (*TNPO*) with pyridine bases

| Donor | Acceptor | |
|---|---|---|
| | *TNB*[a] $K$ [dm$^3$ mol$^{-1}$] | *TNPO* $K$ [dm$^3$ mol$^{-1}$] |
| Pyridine | 0.13 | 9.88 ± 0.14 |
| α-Picoline | 0.09 | 19.87 ± 0.42 |
| β-Picoline | 0.18 | 23.39 ± 0.51 |
| γ-Picoline | 0.23 | 25.60 ± 0.64 |

[a] From Ref. [11]

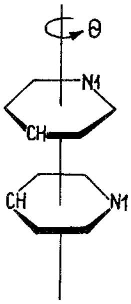

**Fig. 1.** The assumed structure of the sandwich complex (θ = 60°)

A good agreement was achieved (see Table 2) of calculated and experimental energies of *CT* transitions at the angle of $\theta = 240°$ for all complexes with the donors bearing a substituent in their β-positions and $\theta = 120°$ in the other cases. It is interesting that for the complex of *TNPO* with α-picoline the assumption of the existence of two structural isomers allows an agreement between experimental and calculated data.

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## References

[1] Kozioł J., Tomasik P. (1977) Bull. Acad. Polon. Sci. Ser. Sci. Chim. **25**: 689
[2] Kozioł J., Tomasik P. (1979) Bull. Acad. Polon. Sci. Ser. Sci. Chim. **27**: 335
[3] Pietrzycki W., Tomasik P., Kozioł J. (1982) Chem. Script. **20**: 241
[4] Pietrzycki W., Tomasik P., Kozioł J. (1983) Chem. Script. **22**: 159
[5] (a) Katritzky A. R., Randall E. W., Sutton L. E. (1957) J. Chem. Soc. (London): 1769; (b) Sharpe A. N., Walker S. (1961) J. Chem. Soc. (London): 4522; (c) Katritzky A. R., Simmons P. (1960) Rec. Trav. Chim. **79**: 361; (d) Tomasik P. (1974) Pr. Nauk. Inst. Chem. Technol. Nafty Węgla Polit. Wrocław. 19, Ser. Monografie **5**: 44
[6] Gundermann K. D., Alles H. U. (1966) Angew. Chem. Intern. Ed. Engl. **5**: 846
[7] Foster R., Matheson L. B. (1967) Spectrochim. Acta **23 A**: 2037
[8] Benesi H. A., Hildebrand J. H. (1949) J. Am. Chem. Soc. **71**: 1703
[9] Ohta T., Kuroda H., Kuni T. L. (1970) Theoret. Chim. Acta **19**: 167
[10] Mayoh B., Prout C. K. (1972) J. Chem. Soc. Faraday Trans. II **68**: 1072
[11] Foster R. (1969) Organic Charge-Transfer Complexes. Academic Press, New York

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