

SHORT COMMUNICATION

**FTIR study of N–H \cdots π hydrogen bonding:
N-alkylpropanamides – aromatic donor systems**

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Abstract: This paper reports the results of an FTIR study in the region of the fundamental NH stretching vibration for *N*-methyl, *N*-isopropyl, *N*-*tert*-butyl and *N*-1,2,2-trimethylpropanamide – aromatic hydrocarbon systems. In addition to the spectroscopic parameters, the equilibrium constant for the 1:1 N–H \cdots π complexes (at 298 K) are given.

Keywords: hydrogen bonding, *N*-monosubstituted amides, aromatic hydrocarbons.

INTRODUCTION

The present study is a part of our continuing investigations of the hydrogen bonding of *N*-substituted amides.^{1–4} N–H \cdots π hydrogen bonding between four *N*-alkylpropanamides and the aromatic hydrocarbons (benzene, toluene, xylenes, 1,2,3-trimethylbenzene, 1,2,3,5-tetramethylbenzene, ethylbenzene and diethylbenzenes) was examined.

EXPERIMENTAL

N-methyl (NMPA), *N*-isopropyl (NiPPA), *N*-*tert*-butyl (NtBPA) and *N*-1,2,2-trimethylpropanamide (NHPA) were synthesized and purified by redistillation under reduced pressure or by recrystallization. Carbon tetrachloride (spectroscopic grade), benzene, toluene, xylenes, 1,2,3-trimethylbenzene, 1,2,3,5-tetramethylbenzene, ethylbenzene and diethylbenzenes (p.a.) were used without further purification.

The IR spectra in the NH fundamental stretching vibration region were recorded on a Bomem MB100 FT spectrometer, using UVIRSIL (1–5 cm) and KBr (0.05–0.4 cm) cells. Measurements were performed at room temperature (298 K). The concentration of the amides was kept below 0.005 mol dm^{–3}, in order to eliminate amide self-association. The other experimental details were given previously.^{1,3} Since the monomer and complex (NH) bands overlap significantly, the experimental spectra were deconvoluted.

The reported frequencies and half-widths ($\nu_{1/2}$) were reproducible within 0.5 and 1 cm^{–1}, respectively. The integrated molar absorption coefficients (B^0) were obtained to within ± 5 %. The average relative standard deviation of the equilibrium constant was 5 %.

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RESULTS AND DISCUSSION

The spectroscopic characteristics for the monomer (free) $\nu(\text{NH})$ band of the studied amides are given in Table I.

TABLE I. Spectroscopic characteristics of the $\nu(\text{NH})$ band of *N*-alkylpropanamides in dilute CCl_4 solution (at 298 K)

| Amide | $\nu(\text{NH})/\text{cm}^{-1}$ | $\nu_{1/2}/\text{cm}^{-1}$ | $B^0 \times 10^{-6}/\text{cm mol}^{-1}$ |
|--|---------------------------------|----------------------------|---|
| <i>N</i> -methylpropanamide | 3470.9 | 13 | 2.2 |
| <i>N</i> -isopropylpropanamide | 3445.2 | 13 | 1.5 |
| <i>N</i> - <i>tert</i> -butylpropanamide | 3445.1 | 12 | 1.6 |
| <i>N</i> -1,2,2 trimethylpropanamide | 3447.0 | 14 | 1.7 |

The spectroscopic parameters for $\text{N-H} \cdots \pi$ complexes are summarized in Table II. Determination of the equilibrium constant was described earlier¹ and the values for K_{298} are given in Table III.

TABLE II. Spectroscopic parameters of the $\text{N-H} \cdots \pi$ complexes between *N*-alkylpropanamides and the aromatic donors

| Amide | Donor | $\Delta\nu(\text{NH})/\text{cm}^{-1}$ | $\nu_{1/2}/\text{cm}^{-1}$ | $B^0 \times 10^{-6}/\text{cm mol}^{-1}$ |
|----------------------------|----------------------------|---------------------------------------|----------------------------|---|
| NMPA | Benzene | 23 | 16 | 2.8 |
| | Toluene | 30 | 14 | 3.0 |
| | Xylene* | 36 | 13 | 3.3 |
| | 1,2,3-Trimethylbenzene | 41 | 14 | 3.5 |
| | 1,2,3,5-Tetramethylbenzene | 46 | 14 | 3.8 |
| | Ethylbenzene | 30 | 13 | 3.3 |
| | Diethylbenzene* | 36 | 15 | 3.8 |
| | NiPPA | Benzene | 19 | 17 |
| Toluene | | 26 | 16 | 2.3 |
| Xylene* | | 31 | 17 | 2.4 |
| 1,2,3-Trimethylbenzene | | 34 | 14 | 2.7 |
| 1,2,3,5-Tetramethylbenzene | | 41 | 15 | 2.9 |
| Ethylbenzene | | 26 | 17 | 2.5 |
| Diethylbenzene* | | 31 | 14 | 3.0 |
| NtBPA | | Benzene | 17 | 13 |
| | Toluene | 19 | 13 | 2.6 |
| | Xylene* | 24 | 13 | 2.8 |
| | 1,2,3-Trimethylbenzene | 26 | 15 | 3.2 |
| | 1,2,3,5-Tetramethylbenzene | 31 | 15 | 3.3 |
| | Ethylbenzene | 20 | 13 | 2.8 |
| | Diethylbenzene* | 22 | 12 | 3.4 |

TABLE II. Continued

| Amide | Donor | $\Delta\nu(\text{NH})/\text{cm}^{-1}$ | $\nu_{1/2}/\text{cm}^{-1}$ | $B^0 \times 10^{-6}/\text{cm mol}^{-1}$ |
|-------|----------------------------|---------------------------------------|----------------------------|---|
| NHPA | Benzene | 20 | 16 | 3.4 |
| | Toluene | 24 | 16 | 3.5 |
| | Xylene* | 27 | 16 | 3.6 |
| | 1,2,3-Trimethylbenzene | 32 | 16 | 3.7 |
| | 1,2,3,5-Tetramethylbenzene | 35 | 17 | 4.0 |
| | Ethylbenzene | 24 | 16 | 3.5 |
| | Diethylbenzene* | 26 | 16 | 4.2 |

*Data for *o*-, *m*- and *p*-isomers differ by less than the experimental error. The average values are taken.

TABLE III. Equilibrium constants ($\text{dm}^3 \text{mol}^{-1}$) for N-H... π complex formation between *N*-alkylpropanamides and the aromatic donors (at 298 K)

| | NMPA | NiPA | NtPA | NHPA |
|----------------------------|-------|-------|-------|-------|
| Benzene | 0.108 | 0.083 | 0.083 | 0.046 |
| Toluene | 0.121 | 0.085 | 0.090 | 0.055 |
| Xylene* | 0.153 | 0.093 | 0.096 | 0.074 |
| 1,2,3-Trimethylbenzene | 0.163 | 0.108 | 0.108 | 0.083 |
| 1,2,3,5-Tetramethylbenzene | 0.168 | 0.122 | 0.115 | 0.104 |
| Ethylbenzene | 0.134 | 0.094 | 0.084 | 0.071 |
| Diethylbenzene* | 0.156 | 0.100 | 0.101 | 0.083 |

*Data for *o*-, *m*- and *p*-isomers differ by less than the experimental error. The average values are taken.

Inspection of the data in Tables I and II reveals the fact that the $\nu(\text{NH})$ band for the N-H... π complexes is shifted towards lower frequency, relative to the free amides. The halfwidth ($\nu_{1/2}$) and the integrated intensity of the complex band are increased compared with the monomer $\nu(\text{NH})$ band. The frequency shift ($\Delta\nu$) and the difference between the integrated intensities of the complex and monomer band (ΔB^0) increase in the following order of the π -electron donors: benzene < toluene < xylene < 1,2,3-trimethylbenzene < 1,2,3,5-tetramethylbenzene. Also, the spectroscopic effects are more expressed for diethylbenzene compared to ethylbenzene. The presence of methyl groups attached to the benzene ring increases the π -electron density of the aromatic ring, enabling more effective hydrogen bonding with an amide proton. It is obvious that the number of methyl groups present in the aromatic donor molecule increases the stability of the N-H... π complex, as has also been observed for other amides.⁴

Comparison of the data for the studied amides indicates that the stability of the N-H... π complex decreases from *N*-methyl to branched *N*-alkylpropanamides. Steric hindrance of the branched alkyl substituents obviously affects the N-H... π hydrogen bonding ability of the NH proton.

It was shown previously^{3,4} that the charge transfer mechanism can make a significant contribution to N-H... π hydrogen bonding. One of the important indications for the pres-

ence of charge transfer in a hydrogen bond is a linear correlation between the frequency shift function $(\nu_0/\Delta\nu)^{1/2}$ and the donor ionization potential (I_D).^{5,6}

$$I_D = C_1 (\nu_0/\Delta\nu)^{1/2} + C_2$$

where ν_0 represents the frequency for the $\nu(\text{NH})$ monomer band. For the present amide - aromatic donor systems, a good linearity between I_D and $(\nu_0/\Delta\nu)^{1/2}$ was established, with a linear correlation coefficient above 0.99. This fact indicates that charge transfer contributes to the N-H \cdots π hydrogen bonding investigated in this study.

ИЗВОД

ФТИЦ СПЕКТРОСКОПСКО ИЗУЧАВАЊЕ N-H \cdots π ВОДНИЧНЕ ВЕЗЕ: СИСТЕМИ N-АЛКИЛПРОПАНАМИД – АРОМАТИЧНИ ДОНОР

АЛЕКСАНДАР Д. НИКОЛИЋ, МАРКО Р. МЛАДЕНОВИЋ*, ЛАДИСЛАВ ГОБОР, ДУШАН Г. АНТОНОВИЋ*
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У раду се дају резултати ФТИЦ спектроскопског испитивања основне валентне N-H вибрације за растворе четири N-алкилпропанамида и седам ароматичних угљоводоника у угљентетрахлориду. Одређене су константе равнотеже за 1:1 N-H \cdots π комплексе и размотрен је допринос механизма преноса наелектрисања испитиваним водничним везама.

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