

## КРАТКИЕ СООБЩЕНИЯ

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## INTERMOLECULAR HYDROGEN BONDING BETWEEN N-SUBSTITUTED CAPROAMIDES AND TETRAHYDROFURAN

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The results are reported of a study of hydrogen bonding between various N-substituted caproamides and tetrahydrofuran as an O-electron donor by means of FTIR spectroscopy. The spectroscopic characteristics for N—H...O hydrogen bonded complexes are given. The B3LYP functional with 6-31G\*\* basis set has been used to calculate the structural parameters of the studied hydrogen bonded complexes. It can be assumed that both inductive and steric effects play an important role in the stability of these hydrogen bonded complexes.

**Keywords:** hydrogen bonding, N-substituted caproamide, tetrahydrofuran, DFT.

## INTRODUCTION

Hydrogen bonding has a great importance in chemistry and biology. Numerous theoretical and experimental studies have been devoted to hydrogen bonding [ 1—3 ]. Knowledge of N—H...O interactions of N-substituted amides contributes to a better understanding of the structure of polypeptides and proteins. [ 4 ]. In our laboratory, during continuous and extensive research of N-substituted amides and their interactions in solutions, N—H...O, [ 5—8 ] hydrogen bonded complexes were investigated using IR techniques. The application of the B3LYP density functional with various basis sets can provide reasonable information about the geometry and energy of different hydrogen bonded complexes [ 9, 10 ]. In the present work, we investigated the N—H...O interactions of newly synthesised N-alkyl caproamides in order to provide better insight into the nature of the hydrogen bonding of secondary amides.

## EXPERIMENTAL

Various N-monosubstituted caproamides (NsCA) of general formula  $\text{CH}_3(\text{CH}_2)_4\text{CONHR}$ , wherein R is *n*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl, and *n*-pentyl (NPrC, NBuC, NsBC, NiBC, NtBC, NPeC), were synthesised by Schotten-Baumann reaction, by acylation of the corresponding amines with alkyl chloride. The purity of these N-monosubstituted amides was checked by GC and mass spectrometry. Based on the GC results all the samples used in this work had purities 99.2 % or better. Tetrahydrofuran was obtained from commercial sources (Fluka, > 97 %) and was used without further purification.

In order to avoid self-association, amide concentrations in carbon tetrachloride solutions were below  $0.003 \text{ mol} \cdot \text{dm}^{-3}$ . The concentration of tetrahydrofuran varied between  $0.25 \text{ mol} \cdot \text{dm}^{-3}$  and  $1 \text{ mol} \cdot \text{dm}^{-3}$ .

Infrared spectra were obtained using a Thermo-Nicolet Nexus 670 instrument. A DTGS detector was employed in IR measurements. Samples were placed in 1—5 cm (IR) UVIRASIL cells and the measurements were performed at 298 K. The reported frequencies and half-widths were reproducible

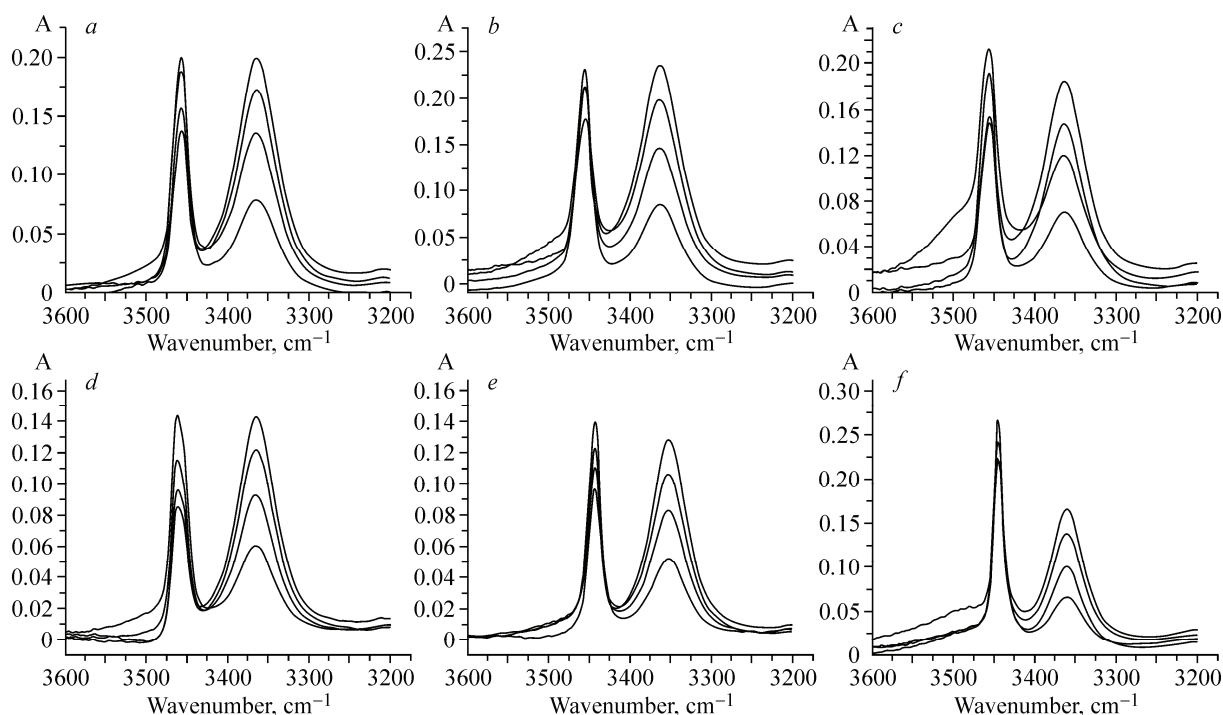


Fig. 1. IR spectra of N-substituted caproamides in the presence of tetrahydrofuran: a) N-propyl caproamide, b) N-butyl caproamide, c) N-*iso*-butyl caproamide, d) N-*sec*-butyl caproamide, e) N-*tert*-butyl caproamide, f) N-pentyl caproamide

within 0.2 and 1  $\text{cm}^{-1}$ , respectively. The integrated molar absorption coefficients were obtained within  $\pm 5\%$ . The equilibrium constants were determined with average relative standard deviation of 6.6%. The formation constants were determined from the monomer absorbancy using Becker's procedure [11].

**Quantum chemical calculations.** Density functional theory with the B3LYP functional [12, 13] was used in combination with the 6-31G\*\* basis set. The Berny algorithm was used for the optimization of the molecular geometry expressed in terms of the bond lengths and valence angles. Standard convergence criteria were used to complete the geometry optimization process. All of the calculations were performed with the Gaussian 09 software package [14].

## RESULTS AND DISCUSSION

Fig. 1 relates to the IR spectra of NsCA in the presence of tetrahydrofuran. The spectroscopic parameters for N—H...O hydrogen bonded complexes obtained by the IR measurements are summarized in Table 1. Fig. 2 shows a graphical determination of the equilibrium constants on the basis of

Table 1

Spectroscopic parameters for N—H...O hydrogen bonded complexes obtained in IR measurements

	$\Delta\nu, \text{cm}^{-1}$	$\nu_{1/2}, \text{cm}^{-1}$	$\varepsilon \cdot 10^{-3}, \text{cm}^2 \cdot \text{mol}^{-1}$	$B^0 \cdot 10^{-6}, \text{cm} \cdot \text{mol}^{-1}$	$(\partial\mu_r/\partial r) \times 10^{20}, \text{c}$
NPrC—THF	94.1	55	130.6	10.6	2.36
NBuC—THF	94.2	55	166.1	13.6	2.86
NiBC—THF	94.7	57	80.1	6.2	1.38
NsBC—THF	91.6	51	124.9	8.5	2.35
NtBC—THF	85.2	46	125.4	7.6	2.14
NPeC—THF	94.2	53	150.4	11.4	3.09

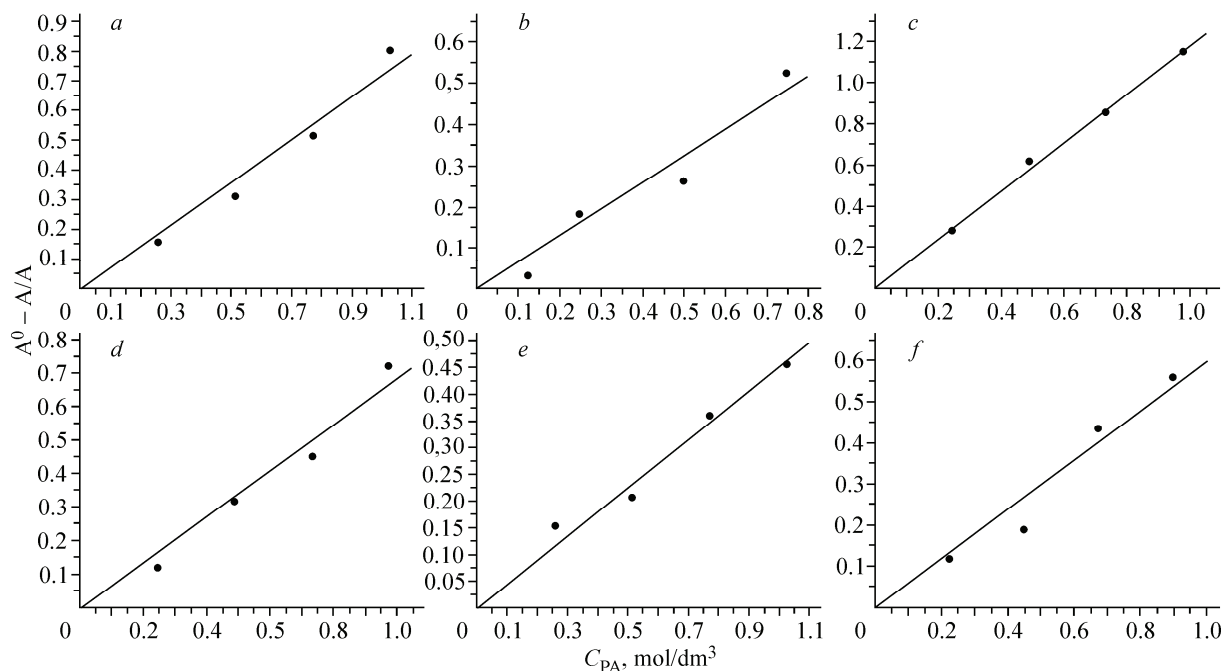


Fig. 2. Geometrically optimized hydrogen bonded complexes of N-substituted caproamides with tetrahydrofuran a) N-propyl caproamide, b) N-butyl caproamide, c) N-*iso*-butyl caproamide, d) N-*sec*-butyl caproamide, e) N-*tert*-butyl caproamide, f) N-pentyl caproamide

the Beceker method. The equilibrium constant values and accuracy parameters for the equilibrium constants determination are given in Table 2. In order to evaluate the contribution of the charge transfer mechanism, the intermolecular transition moments were calculated from the difference in the integrated intensities for the free and hydrogen bonded N—H groups [ 15 ], and are also presented in Table 1.

$$\frac{\partial \mu_t}{\partial r} = \sqrt{\frac{3000mc^2}{Na\pi}} \left( \sqrt{B_{hb}^0} - \sqrt{B_f^0} \right), \quad (1)$$

where  $B_{hb}^0$  and  $B_f^0$  are the integrated intensities of the bands of hydrogen bond and free NH groups;  $m$  is the reduced mass of the NH oscillator;  $c$  is the velocity of light; and  $Na$  is the Avogadro number.

The obtained IR spectroscopic parameters clearly indicate N—H···O hydrogen bonding between N-substituted caproamides and the tetrahydrofuran. Comparison of the **equilibrium** constants as well as the frequency shift values for the series of examined amides shows that the most stable complex with tetrahydrofuran is formed by N-isobutyl caproamide while the least stable complex is formed by N-*tert* butyl caproamide.

In the case of a significant contribution by the charge transfer mechanism, for the series of proton donors, a positive correlation between the intermolecular transition moments and relative frequency shift can be observed, according to the equation [ 15 ]

$$\frac{\partial \mu_t}{\partial r} = Q \frac{\Delta \nu}{\nu_0}. \quad (2)$$

For the series of amides examined in this study, a correlation between the intermolecular transition moments and relative frequency shift, which would indicate a contribution from the charge transfer mechanism, was not observed.

Table 2

The equilibrium constants obtained in IR measurements, determination coefficients and standard deviations

	K, dm <sup>3</sup> ·mol <sup>-1</sup>	R <sup>2</sup>	SD
NPrC—THF	0.73	0.9907	0.057
NBuC—THF	0.61	0.9764	0.052
NiBC—THF	1.11	0.9795	0.052
NsBC—THF	0.69	0.9981	0.023
NtBC—THF	0.47	0.9915	0.051
NPeC—THF	0.59	0.9863	0.027

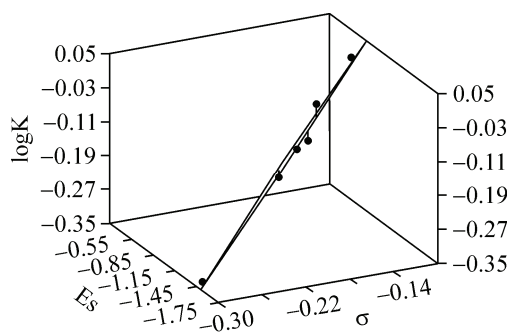


Fig. 3. Plot of  $\log K_{298}$  versus Taft steric,  $E_S$  and inductive  $\sigma^*$  substituent constants

The stability of hydrogen bond complexes increases in the order: NtBC < NPeC < NBuC < NsBC < NPrC < NiBC. Differences in the stability of the N—H...O complexes for the six studied N-substituted caproamides can be interpreted using the Taft equation [ 16 ]

$$\log K_{298} = \log K_{298}^0 + \rho \sigma^* + \delta E_S, \quad (3)$$

where  $\log K_{298}^0$  represents the formation constant of N-

methyl caproamide,  $\sigma^*$  and  $E_S$  represent inductive and steric factors for alkyl groups. If  $\log K_{298}$  is correlated with both  $\sigma^*$  and  $E_S$  a good correlation is obtained

$$\log K_{298} = 0.1145 + 3.537\sigma^* - 0.3956E_S, \quad R = 0.975. \quad (4)$$

Good correlation with both  $\sigma^*$  and  $E_S$ , indicates that both inductive and steric effects are important in hydrogen bonded complex formation. Several investigators [ 17—19 ] have obtained equilibrium constants for hydrogen bonding between phenols with various (cyclic and acyclic) ethers and have established that donor-acceptor interactions are sensitive to both steric and electronic effects.

The equilibrium constants for N-methyl formamide, N-methyl propionamide, N-methyl trichloroacetamide-tetrahydrofuran complexes [ 6, 8, 20 ] have higher values than the constants obtained in this study.

The geometrically optimized hydrogen bonded complexes are shown in Fig. 4. The structural parameters of the hydrogen bonded complexes computed at the DFT (B3LYP)/6-31G\*\* level are presented in Table 3.

The correlation coefficients between the parameters obtained by FTIR spectroscopy and DFT calculations are presented in Table 4. The significance of the reported correlation coefficients was tested

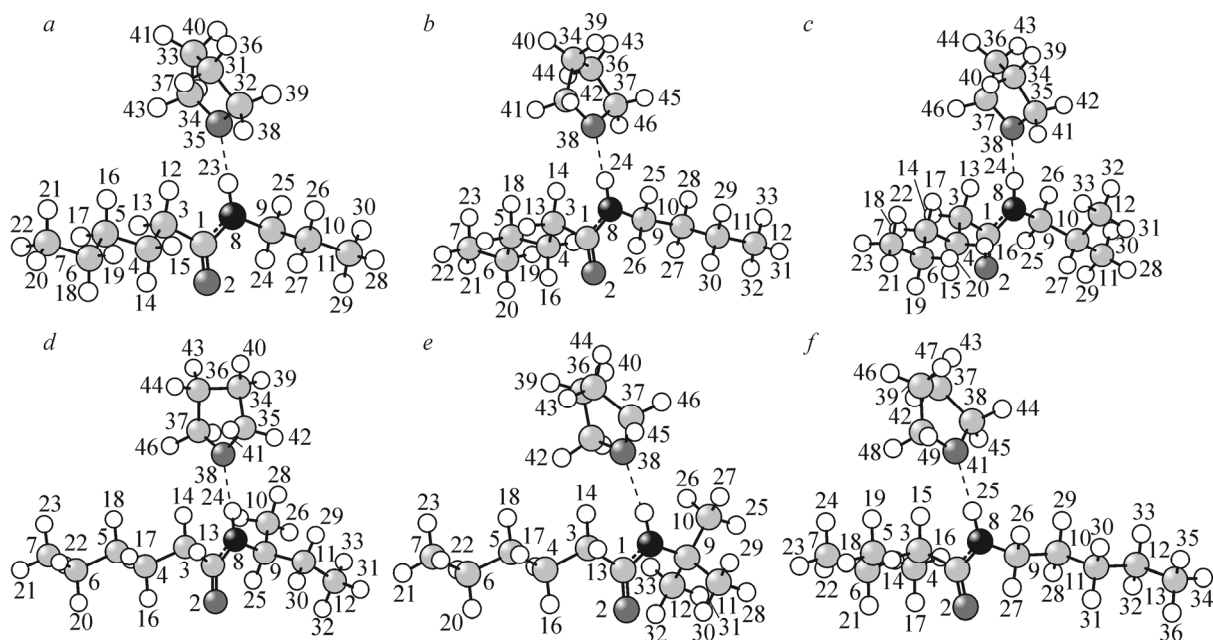


Fig. 4. Graphical determination of the equilibrium constants on the basis of the Beceker method: *a* — N-propyl caproamide, *b* — N-butyl caproamide, *c* — N-iso-butyl caproamide, *d* — N-sec-butyl caproamide, *e* — N-tert-butyl caproamide, *f* — N-pentyl caproamide,  $C_{PA}$  — concentration of proton acceptor THF

Table 3

Selected geometrical parameters obtained from the (B3LYP/6-31G\*\*) calculations for the optimized structure of the *N*-substituted caproamide complexes

	C—N distance, Å	N—H distance, Å	$r(\text{H}\cdots\text{O})$ distance, Å	$r(\text{N—H}\cdots\text{O})$ , distance, Å	$\alpha(\text{N—H}\cdots\text{O})$ angle, deg.
NPrC—THF	1.362	1.015	2.001	3.015	174.9
NBuC—THF	1.362	1.015	2.002	3.017	176.7
NiBC—THF	1.362	1.015	1.999	3.014	176.2
NsBC—THF	1.361	1.016	2.005	3.021	175.1
NtBC—THF	1.361	1.016	2.033	3.049	172.6
NPcC—THF	1.362	1.015	2.004	3.019	176.6

Table 4

Correlation coefficients between spectroscopic and theoretical hydrogen bond parameters

	$r(\text{C—N})$	$r(\text{N—H})$	$r(\text{H}\cdots\text{O})$	$r(\text{N—H}\cdots\text{O})$	$\alpha(\text{N—H}\cdots\text{O})$
$\Delta\nu$	0.832	-0.832	-0.977*	-0.982*	0.914
$\nu_{1/2}$	0.856	-0.856	-0.928	-0.935	0.824
$\varepsilon$	0.118	-0.118	0.024	0.018	0.202
B	0.456	-0.456	-0.315	-0.324	0.480
K	0.422	-0.422	-0.613	-0.612	0.418
$\partial\mu_i/\partial r$	0.153	-0.153	-0.067	-0.074	0.294

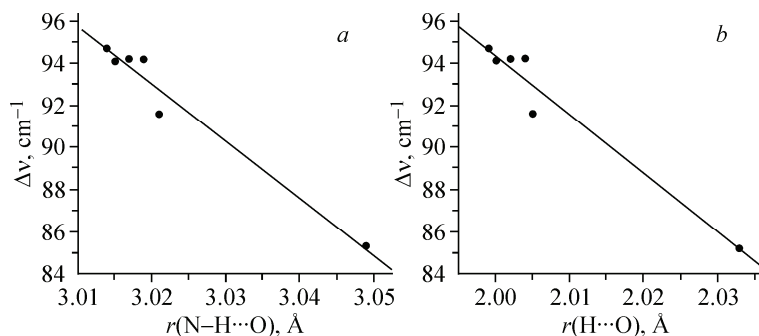
with a *t* test at significance level  $P < 0.01$ . Fig. 5 relates to the linear correlation of frequency shift  $\Delta\nu$  (N—H) with the N—H $\cdots$ O distance (*a*), H $\cdots$ O distance (*b*).

As can be seen from Table 4, the experimental parameter which most significantly correlates with the theoretical parameters is the frequency shift  $\Delta\nu$  (N—H). It is well-known that the frequency shift is negatively correlated with the length and positively with the strength of the hydrogen bond [21]. Correlations of frequency shift with experimentally and theoretically obtained geometrical parameters were found for a number of different hydrogen bonded complexes [22—24]. Stronger hydrogen bonds are shorter and cause larger red shifts in the IR spectra.

### CONCLUSIONS

In this work FTIR spectroscopic and DFT theoretical parameters were obtained for hydrogen bonds of six investigated *N*-substituted caproamides with tetrahydrofuran. Correlations between the experimental and theoretical parameters were observed. Based on the obtained data and the correlations, it can be concluded that for the series of examined caproamides, there is no significant influence

Fig. 5. Linear correlation of the frequency shift  $\Delta\nu$  (N—H) with the N—H $\cdots$ O distance (*a*), and the H $\cdots$ O distance (*b*)



from the charge transfer mechanism on the stability of the complexes. It can be assumed that both inductive and steric effects play an important role in the stability of these hydrogen bonded complexes.

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