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Synthesis and FTIR spectroscopic study of some *N*-monosubstituted propanamides

D.G. Antonović[a], N.D. Stojanović[a], B.M. Božić[a], A.D. Nikolić[b], S.D. Petrović[a,*]

[a]*Department of Organic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O. Box 494, YU-11000 Belgrade, Yugoslavia*
[b]*Institute of Chemistry, Faculty of Science, University of Novi Sad, YU-21000 Novi Sad, Yugoslavia*

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Abstract

In the present work we investigated the conformations of some *N*-mono-substituted propanamides of general formula CH_3CH_2CONHR, wherein R is chosen from *n*-(C_1–C_9)alkyl, cyclo(C_3–C_6)alkyl, some branched (C_3–C_6)alkyl or phenyl. The amides were synthesised by the well known Schotten–Baumann reaction—acylation of the corresponding amines with propionyl chloride. On the basis of FTIR data for diluted solutions (concentrations below 10^{-3} mol dm^{-3}) of *N*-mono-substituted propanamides in carbon tetrachloride, chloroform, dichloromethane, or a 1:1.5 mixture of benzene and carbon tetrachloride the exact position of the N–H stretching band was established. For spectroscopic data the different conformational isomers were assigned and its structures unequivocally proven. These results are in good accordance with ^{1}H NMR and MS data. © 1997 Elsevier Science B.V.

Keywords: Conformational isomers; FTIR spectroscopy; *N*-Monosubstituted propanamides; N–H stretching band

1. Introduction

This paper is a part of a continuing and extensive study of *N*-monosubstituted amides and their behaviour in solution [1–5]. The structural character and nature of the molecular association of amides are of particular interest because of the importance of amides in biological systems.

In very dilute solutions secondary amides studied under low resolution show only one band in the 3460–3420 cm^{-1} range [6–10]. Under conditions of high resolution this band can often be split into two components. The twin bands shown by most secondary amides have therefore been assigned to the *cis* and *trans* rotational isomers, and it becomes possible to estimate the relative proportions of the two by comparison of their relative intensities.

Numerous spectroscopic and theoretical studies of ^{N}-monosubstituted amides of the type of R–CONH–R have been reported [11–17]. Most of these spectroscopic studies have been carried out in the presence of another medium, either apolar solvents where association can occur even at low concentrations [11], in the

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* Corresponding author. Tel: +38 111 322 6146; fax: +38 111 322 0847.

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Table 1
The N–H stretching frequencies of *N*-monosubstituted propanamides of general formula CH_3CH_2CONHR in various solvents

No.	R	$\nu_{(N-H)}$ (/cm^{-1})			
		CCl_4	$CHCl_3$	CH_2Cl_2	$C_6H_6 + CCl_4$
1	Methyl	3471.6	3456.8	3460.0	3447.8
2	Ethyl	3458.1	3450.4	3446.5	3438.3
3	*n*-Propyl	3458.1	3450.4	3446.5	3438.5
4	Isopropyl	3444.6	3440.8	3435.0	3425.0
5	*n*-Butyl	3456.2	3450.4	3446.5	3436.4
6	*sec*-Butyl	3442.7	3436.9	3433.0	3420.7
7	Isobutyl	3463.9	3454.2	3448.5	3438.9
8	*tert*-Butyl	3444.6	3440.8	3436.9	3426.3
9	*n*-Pentyl	3456.2	3450.4	3446.5	3438.0
10	3-Methylbutyl	3456.2	3450.4	3444.6	3435.2
11	*n*-Hexyl	3456.2	3450.4	3446.5	3436.4
12	1,2,2-Trimethylpropyl	3446.5	3442.7	3437.0	3427.1
13	*n*-Heptyl	3456.2	3450.4	3446.5	3436.6
14	*n*-Octyl	3456.2	3450.4	3446.5	3435.4
15	*n*-Nonyl	3456.2	3450.4	3446.5	3436.4
16	Cyclopropyl				
	trans	3448.5 (93.4%)	3444.6 (92.4%)	3439.0 (92.0%)	3424.2 (100%)
	cis	3411.8 (6.6%)	3404.1 (7.6%)	3401.0 (8.0%)	–
17	Cyclobutyl	3446.5	3440.8	3436.9	3423.6
18	Cyclopentyl	3446.5	3440.8	3436.9	3428.0
19	Phenyl				
	trans	3442.7 (97.4%)	3435.0 (98.8%)	3427.2 (100%)	3417.0 (100%)
	cis	3398.3 (2.6%)	3387.0 (1.2%)	–	–

vapour phase with a carrier gas [12], or in low-temperature matrices [13]; gas-phase infrared spectra of substituted alkylamides have also been acquired [18].

The mean degree of association of hydrogen-bonded *N*-methylpropanamide molecules was estimated in the liquid phase from the NMR chemical shift of free and hydrogen-bonded N–H protons in an NMR study of the chain association of *N*-methylpropanamide molecules [19].

A detailed low-temperature matrix-isolation infrared study of acetamide was recently conducted by Kunsen et al [20].

2. Experimental

Various *N*-monosubstituted propanamides, of general formula CH_3CH_2CONHR, wherein R is methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n* -octyl, *n*-nonyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, isopropyl, isobutyl, *sec*-butyl, *tert*-butyl, phenyl, 3-methylbutyl or 1,2,2-trimethylpropyl, were synthesised by the well known Schotten–Baumann reaction of acylation of the corresponding amines with propionyl chloride. The reactions were performed in the presence of potassium hydroxide which was added to remove the HCl evolved in the reaction. The purity of these *N*-monosubstituted propanamides was checked by GC and mass spectrometry. For all samples used in this work the purities as judged by GC were 99.2% or better.

^{1}H NMR spectra of solutions in $CDCl_3$ were determined with a Varian EM390 (90 MHz) instrument using tetramethylsilane as internal standard.

Mass spectra were acquired on a type 311 A reversed-geometry mass spectrometer (Varian MAT, Bremen, FRG), using a direct probe and 70 eV ionising energy.

IR spectra were recorded on a Bomem MB 100 FTIR spectrophotometer with 1-cm UVIRSIL sample cell (Norel, Inc., USA).

3. Results and discussion

We investigated solutions of *N*-monosubstituted propanamides in CCl_4, $CHCl_3$, CH_2Cl_2 and in a mixture of C_6H_6 and CCl_4 (1:1.5). Concentrations were 3.5×10^{-3} mol dm^{-3} and the position of the N–H stretching band was determined with an accuracy of $\pm$ 0.01 cm^{-1}.

The FTIR spectroscopic data of the *N*-monosubstituted propanamides investigated are given in Table 1.

In dilute carbon tetrachloride solutions (below 7×10^{-3} mol dm^{-3}) *N*-mono-substituted propanamides exist as monomers as detailed in our previous work[1].

The data listed in Table 1 show that for the series of *N*-(*n*-alkyl)propanamides it is evident that increasing hydrocarbon chain length does not influence the position of the N–H stretching band. On the other hand, the branching of substituents reduces the frequencies. The existence of *cis* rotamers in minor quantities is evident only in *N*-cyclopropyl- and *N*-phenylpropanamide. Also, the presence of *N*-cycloalkyl groups reduces $\nu_{(N-H)}$ stretching frequencies.

On the basis of IR spectroscopic results from solutions of the investigated *N*-mono-substituted propanamides in various halogenated solvents (chloroform, dichloromethane) it was concluded that there is a weak hydrogen-bonding interaction between the solvent proton-donor ($CHCl_3$ and CH_2Cl_2) and the investigated amides. We also noticed that the proportion of the *trans* isomer decreases with solvent polarity ($CH_2Cl_2 > CHCl_3 > CCl_4$). The observed difference between halogenated solvents ($CHCl_3$ and CH_2Cl_2) and benzene for hydrogen bonding with amides has been explained in terms of the additional possibility of formation of the $NH \cdots \pi$ hydrogen bond in benzene solutions.

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