

CP/MAS, ^{13}C AND ^{17}O NMR STUDIES OF PROTON TRANSFER AND DYNAMICS OF CYANOPYRIDINE HYDROGEN-BOND COMPLEX WITH TRICHLOROACETIC ACID IN CRYSTAL AND IN SOLUTION*

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Received 21 June 2005

The hydrogen bond (H-bond) in the complex of cyanopyridine (4-pyridincarbonitrile, $\text{C}_6\text{H}_4\text{N}_2$, further CyPy) with trichloroacetic acid (TCA) was investigated in the solid state and in the solution (1 M in CH_3CN). The ^{13}C CP/MAS results as well as X-ray and neutron diffraction reveal a complete proton transfer (CPT) for the CyPy-TCA complex. An experimental criterion of the threshold of CPT is proposed. Reorientational dynamics of ‘free’ and ‘bonded’ CyPy molecules in solution were investigated by ^{17}O and ^{13}C NMR relaxation time and nuclear Overhauser effect (NOE) factor measurements. The rotational diffusion even of ‘free’ CyPy molecules is anisotropic, with a corresponding correlation time of 3 ps for rotation and that of 6 ps for tumbling at 293 K. The formation of the CyPy-TCA H-bond complex causes a general slowdown of the overall rotational motion with a very slight increase in its anisotropy (7 ps for rotation and 17 ps for tumbling, respectively). The results are compared with similar data on H-bonding in pyridine N-oxide/acid systems.

Keywords: hydrogen bonding, NMR shifts and relaxation, pyridine

PACS: 33.15.Fm, 76.60.-k, 33.70.Jg

1. Introduction

Derivatives of pyridine (Py) and pyridine N-oxide (PyO) are of particular interest for the study of hydrogen bonds [1–5]. Their proton accepting properties can be considerably varied by a proper substitution in certain position of the π -electron ‘carcass’ of these molecules. Hence one can manipulate the H-bond strength and thus gain or damp the proton transfer and its dynamics. The discussion on these problems has been boosted recently by the ideas of the role of H-bond in important enzymatic reactions [6, 7]. Also note that pyridine N-oxide is one of possible reference (standard) substances of the H-bond strength scale.

Obviously, the single crystal neutron diffraction would provide the most authentic information on the geometry of hydrogen bonds. On the other hand, however, the crystals suitable for neutron diffraction as well as the technique itself are not always available. Hence, the empirical correlations between the precise H-bond

parameters that are difficult to access and the ‘easily measurable’ quantities are of high practical value. Most spectral parameters (chemical shifts, signal half widths, etc.) can be considered as those ‘easily measurable’ quantities. Although there can be exceptions, e. g. the NMR signals of nuclei of low natural abundance, or some NMR solid-state techniques, which both need a huge amount of data to be sampled and averaged.

This work is a part of general project with the aim to follow the proton transfer in the region close to the middle of the H-bond. In this paper we report the new data concerning the peculiarities of proton shared H-bond with incipient proton transfer between cyanopyridine (4-pyridincarbonitrile, $\text{C}_6\text{H}_4\text{N}_2$, further CyPy) and trichloroacetic acid (TCA) in the crystalline state and in the solution using NMR methods. Reorientational dynamic of ‘free’ and ‘bonded’ CyPy molecules in solution has been investigated by the ^{17}O and ^{13}C NMR relaxation time and nuclear Overhauser effect (NOE) factor measurements. In order to follow the effect of increasing strength of H-bond, some additional ^{13}C NMR shift measurements have been

* The report presented at the 36th Lithuanian National Physics Conference, 16–18 June 2005, Vilnius, Lithuania.

performed on the solutions of CyPy with methanesulfonic acid. The results are compared with similar data on H-bonding of pyridine N-oxide.

2. Experimental

2.1. Samples

Commercial acetonitrile (AN), cyanopyridine (CyPy), trichloroacetic and methanesulfonic acids (TCA and MSA) were preliminary purified by standard methods. Freshly distilled AN was degassed by bubbling argon into the tube and by 3 cycles of N₂ vacuum flushing under sonication. The solution of concentration 1 M of CyPy/TCA in 1:1 ratio was prepared in a dry box by weighing (± 0.1 mg) the components.

2.2. NMR measurements

¹³C and ¹⁷O NMR experiments were carried out on Varian Unity Plus 300 NMR spectrometer at 293 K. The temperature was controlled with an accuracy of ± 0.5 K. All ¹³C NMR measurements were performed in 5 mm tubes. The spin-lattice relaxation times T_1 have been measured by the inversion-recovery pulse sequence $\pi - \tau - \pi/2$ in the usual way. The T_1 values have been determined at 12 different time intervals τ with delay $\geq 10T_1$. A three parameter fitting of peak heights has been used for the calculation of T_1 values. 120 scans were used for each T_1 and 240 for each NOE factor measurement. In order to get better signal-to-noise ratio the natural abundance ¹⁷O spectra were recorded using 10 mm tubes. The number of scans varied from $5 \cdot 10^5$ to $2 \cdot 10^6$.

¹³C cross polarization/magic angle spinning (CP/MAS) spectra of solids were obtained using a Doty dynamic angle-spinning (DAS) probe. Monocrystals of CyPy/TCA were ground and put into a ceramic rotor of DAS in a dry box. For MAS spectra the sample-spinning rate was usually 2–4 kHz, and the error in the spinning rate was less than ± 10 Hz. The CP/MAS pulse sequence is shown in Fig. 1. The most optimal values of parameters were found: the proton $\pi/2$ pulse width $t_{\pi/2}$ of 9 μ s at the pulse power $tpwr$ of 57 dB, the cross-polarization contact time $t_{cnt} = 4095$ μ s, and the decoupler linear modulator setting *dipolar* during acquisition was 4095.

The NMR spectra were processed digitally using the *MestRe-C* [8] and *Microcal Origin* [9] program packages.

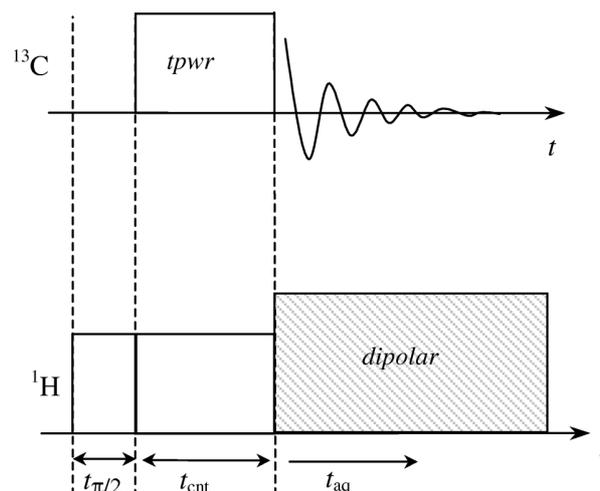


Fig. 1. ¹³C CP/MAS pulse sequence. Parameter values are given in text.

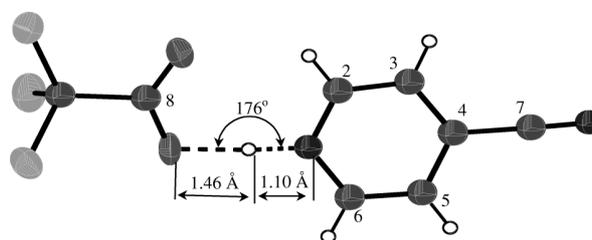


Fig. 2. The structure of CyPy·TCA complex in crystalline phase showing 50% probability displacement ellipsoids and H-bond parameters (X-ray diffraction data at 300 K). For more experimental details and structure refinement procedure see [11].

3. Results and discussion

Very recent investigations of the H-bond complex of CyPy·TCA in the crystal and in solutions by FTIR, neutron and X-ray diffraction techniques [10, 11] evidence the unique form of H-bond in the crystalline phase, namely, the CyPy·TCA complex with complete proton transfer (CPT). The molecular structure of the complex is displayed in Fig. 2. Proton-sharing properties of H-bond investigated by CyPy ring modes in FTIR spectra in solution revealed a rather complicated competition between processes of two sorts of complex formation (CPT and proton-shared hydrogen bond with incipient proton transfer, PSHB) and self-association of acid [11]. Moreover, these FTIR data indicate that in the liquid state CyPy molecules are ‘more’ protonated (‘more’ ionic) than in the crystal.

Since we have dynamical processes that obviously are fast in the time scale of NMR, the variety of H-bond structures is averaged, and thus it is interesting to evaluate the capabilities of this method for the systems studied. Let us start from the ¹³C NMR chemical shift

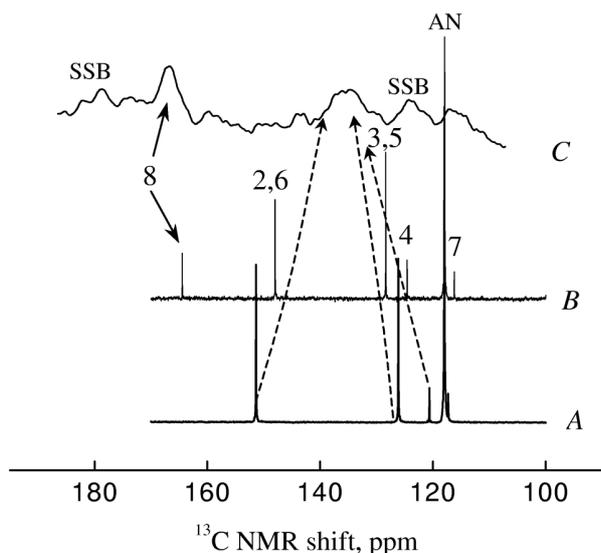


Fig. 3. ^{13}C NMR spectra of 'free' CyPy (A), complex CyPy-TCA (B) in 1 M solution in AN, and CP/ MAS spectrum of CyPy-TCA crystal (C). The numbering of carbons is the same as in Fig. 2; SSB is spinning side bands and AN is signal of $-\text{C}\equiv\text{N}$ group of solvent molecules.

analysis. In the case of PyO interactions with the same acids [12] the electronic charge displacement between the NO moiety and the ring reflects on the large ^{13}C NMR shifts of the *p*-carbon, and these shifts relative to 2, 6- and 3, 5-carbons are good indicators of PT. The ^{13}C NMR spectra of CyPy and CyPy-TCA in solution together with the CP/ MAS spectrum of CyPy-TCA crystal are presented in Fig. 3. The H-bonding causes a decrease of the chemical shift of 2, 6-carbons and has an opposite effect for 3, 5- and 4-carbons. In the crystal, where as we know now very strong CPT complexes are 'frozen' (Fig. 2), all these signals coalesce to one broad contour at 130–140 ppm. Positions of $-\text{COOH}$ and $-\text{C}\equiv\text{N}$ carbon signals (i. e. C_8 and C_7 , according to the numbering in Fig. 2) are practically identical in solution and in the crystalline state. In order to follow the effect of increasing strength of H-bond some additional ^{13}C NMR shift measurements have been performed on the solutions of CyPy with MSA. This very strong acid has been chosen because according to FTIR data [11] the CPT definitely takes place in the CyPy.MSA complex in solution.

The summary of the ^{13}C NMR results of the H-bond in CyPy-acid systems is displayed in Fig. 4. The related data on PyO with the same acids are added for comparison. The interpretation of H-bond based on the ^{13}C NMR shifts of PyO is straightforward. The $\text{C}_{2,6}$ and $\text{C}_{3,5}$ ^{13}C NMR signals look rather 'frozen', like certain reference lines, whereas the C_4 peak moves depending on the H-bond strength (Fig. 4). This al-

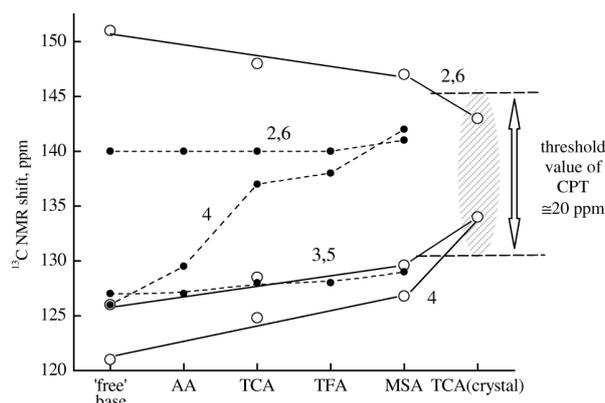


Fig. 4. Monitoring of H-bond in CyPy-acid complexes by ^{13}C NMR spectroscopy (○). Carbon numbering is the same as in Fig. 2. Dashed area symbolizes a merger of ^{13}C NMR signals in CP/ MAS spectrum (Fig. 3). Some data on PyO complexes with the same acids and in addition with acetic (AA) and trifluoroacetic (TFA) ones (●) are presented for comparison. See comments concerning the threshold value of CPT in text.

lows one to formulate a very simple experimental criterion for monitoring the proton transfer to PyO oxygen [12]. In CyPy the chemical shifts of all signals depend on a bonding partner, and thus it is not obvious how to define the thresholds for PSHB turning into CPT. This difference in ^{13}C NMR shift behaviour of Py and PyO ring carbons can be due to several reasons. Much larger ^{13}C NMR shifts of $\text{C}_{2,6}$ and $\text{C}_{3,5}$ carbons can be caused by a stronger disturbance of the electronic structure of the Py ring due to a 'shorter' way to act on the ring via direct H-bond attack on the nitrogen atom than via the extra chemical bond $\text{N}\rightarrow\text{O}$ in PyO molecules (i. e. the bonding $\text{N}\rightarrow\text{O}\cdots\text{HO}$). Another factor is a cyano-substitution of *p*-carbon, i. e. C_4 . Moreover, the tendency of acids to 'self-associate' is much less pronounced in the case of PyO as a bonding partner. Multiple equilibrium processes can average certain factors of electronic structure that are in charge for magnetic screening of nuclei in molecules. Hence, at the present state of investigations, only a rather rough experimental criterion of the threshold of CPT in Py systems can be proposed, namely, $\delta(\text{C}_{2,6}) - \delta(\text{C}_{3,5}) \leq 20$ ppm (Fig. 4).

Besides the chemical shifts, it is also interesting to take a look at the rotational dynamics of CyPy and its complexes with acids. The rotational correlation time τ_c values can be determined by several independent experiments, e. g. from Raman band shape analysis [13] or from NMR relaxation data by determining the dipole-dipole $^{13}\text{C}-^1\text{H}$ contribution ($1/T_{1\text{DD}}$) to the

total relaxation rates ($1/T_1$) of ‘suitable’ ^{13}C nucleus [14]:

$$\frac{1}{T_{1\text{DD}}} = \frac{\eta_{\text{CH}}}{\eta_{\text{max}} T_1} = \left(\frac{\mu_0}{4\pi}\right)^2 \left(\frac{h}{2\pi}\right)^2 \frac{\gamma_{\text{C}}^2 \gamma_{\text{H}}^2}{r_{\text{CH}}^6} N_{\text{H}} \tau_c, \quad (1)$$

where η_{CH} is the NOE factor, η_{max} is the maximum NOE factor (for ^{13}C – ^1H interaction $\eta_{\text{max}} = 1.99$), N_{H} is the number of hydrogen atoms bound to carbon, and r_{CH} is the CH distance. The word ‘suitable’, used just above, means that the motion of the ^{13}C – ^1H vector has not to be involved in internal rotations, i.e. it must characterize the reorientation of the whole molecule or complex.

The ^{13}C relaxation and NOE data of CyPy and its H-bonded complexes are presented in Table 1. According to evaluations [15, 16], the τ_c values based on the T_1 and η_{CH} values measured with a precision of $\pm 5\%$ can be calculated with an accuracy of ± 7 – 8% only. Not all T_1 data are useful to elucidate the rotational dynamics, i.e. to calculate τ_c (Table 1). The dipole–dipole contribution to the total relaxation rates is sufficient for ^{13}C nuclei directly bonded to other ones having nonzero dipole moments, e.g. ^1H , ^{19}F , etc. In the cases of indirect bonding of ^{13}C to dipolar nuclei it can be evaluated by using computational refinements as in [17, 18]. But on the other hand, additional uncertainties are introduced if the molecular geometry is known not precisely enough, and the internal motion cannot be neglected.

The measured $T_{1\text{DD}}$ and η_{CH} values for $-\text{COOH}$ carbons (carbon 8, Table 1) are comparable with $T_{1\text{DD}} = 91$ s, $\eta_{\text{CH}} = 0.45$ for benzoic acid and η_{CH} of 0.8 for the benzoate anion ($\text{C}_6\text{H}_5\text{COO}^-$) [15, 16]. But the main contribution to the relaxation for these nuclei is due to screening anisotropy, whereas the DD and spin-rotation ones contribute only about 20% to the total. Hence these data were not used in further processing.

The direct (and most precise) relaxation data on 2, 6- and 3, 5-carbons of CyPy provide the information about reorientational motion around the ‘long’ axis of molecules. The calculated values $\tau_c \approx 3$ ps for ‘free’ CyPy (Table 1) are comparable with τ_c of 2.8 ps that has been obtained for benzene molecules in the liquid state (298 K) by Raman band shape analysis [13] and with analogous data for PyO systems by ^{13}C NMR [12]. After the addition of acid molecules as partners to form hydrogen bonds, the rates of reorientation around the ‘long’ axis of the complex slightly decrease (τ_c increases from 3 to 4 ps for CyPy·MSA and to 7 ps for CyPy·TCA). The remarkable slowdown for the com-

plex with TCA is explained by the increase of moment of inertia due to ‘heavy’ chlorine atoms. On the other hand, it indicates that the CyPy·TCA complex rotates in solution as a ‘rigid rod’.

The information concerning the tumbling of CyPy and its complexes is more difficult to access. This kind of motion should most effectively reflect on the relaxation of 4-carbon, but only if it is bonded with hydrogen, i.e. in dipolar nuclei. Such is the case of PyO·acid [12], and it might be with Py complexes. But the calculation of τ_c for tumbling motion is not feasible due to cyano-substitution in CyPy molecules. Of course, the relaxation data of $^{-13}\text{C}\equiv^{14}\text{N}$ carbon can be used for this purpose. The main hindering is the very low values of NOE factors for this coupling, e.g. $(\eta_{\text{CN}})_{\text{max}} = 0.14$. According to practical recommendations [14], the precise T_1 and NOE measurements can take 2–3 days. Unfortunately, CyPy/TCA complex in solution was chemically not stable over that period.

It was decided to evaluate the parameters of tumbling dynamics using ^{17}O NMR relaxation data of carboxylic oxygen of TCA. It is well known that for quadrupolar nuclei in liquids their longitudinal relaxation is almost entirely due to the interaction between the nuclear quadrupole moment Q and the electric field gradient at the nucleus [15–18]. In the case of extreme narrowing limit the relaxation rates and the line width at the half height of the NMR signal ($\Delta\nu_{1/2}$) are related by

$$\frac{1}{T_{1,Q}} = \frac{1}{T_{2,Q}} = \pi \Delta\nu_{1/2} = \frac{3\pi^2}{10} \frac{2I+3}{I^2(2I-1)} \chi_{\text{eff}}^2 \tau_c, \quad (2)$$

where an ‘effective’ coupling constant

$$\chi_{\text{eff}} = \chi \sqrt{1 + \frac{\eta^2}{3}} \quad (3)$$

is exploited ($\chi = eQq_{zz}/h$ is the nuclear quadrupole coupling constant, q_{zz} is the largest principal component of EFG tensor, and $\eta = |q_{xx} - q_{yy}|/q_{zz}$ is its asymmetry parameter). This is because q_{zz} and η cannot be evaluated in liquids separately.

It has been found that practically in all cases of carboxylic oxygen (i.e. ^{17}O nuclei, $I = 5/2$) in various H-bonded systems the values of χ_{eff} are between 7.5 and 9.2 MHz [12]. They also match rather well with the corresponding data of benzoic acid in solutions [15, 16], solid carboxylic acids [19, 20], as well as with the results of theoretical calculations [21, 22]. All these ‘well matching’ χ_{eff} values have been obtained from (2) using experimentally measured $\Delta\nu_{1/2}$

Table 1. ^{13}C NMR relaxation and NOE data for CyPy hydrogen bond complexes ^a.

carbon ^b	δ , ppm	T_1 , s	η_{IS}	$T_{1\text{DD}}$, s	τ_c , ps
'free' CyPy					
2,6	151.4	13.43±0.15	1.58±0.01	16.88	2.9
3,5	126.1	13.48±0.07	1.66±0.03	16.14	3.0
4	120.7	68.15±0.94	0.53±0.03	–	–
7	117.3	46.4±1.7	–	–	–
CyPy·TCA					
2,6	147.8	6.56±0.11	1.73±0.01	7.53	6.5
3,5	128.5	6.52±0.07	1.93±0.03	6.72	7.3
4	124.8	31.8±2.9	0.50±0.08	–	–
7	116.2	16.65±0.76	–	–	–
8	164.5	30.5±1.2	0.60±0.06	101	–
CyPy·MSA					
2,6	147.0	8.6±0.3	1.07±0.06	15.9	3.0
3,5	129.6	10.1±0.3	1.64±0.14	12.2	4.0
4	126.8	35.9±4.8	0.06±0.05	–	–
7	116.1	25.7±4	–	–	–

^a In 1 M solution in AN at 293 K, except CyPy·MSA in 0.125 M solution at 323 K.

^b For numbering, see Fig. 2.

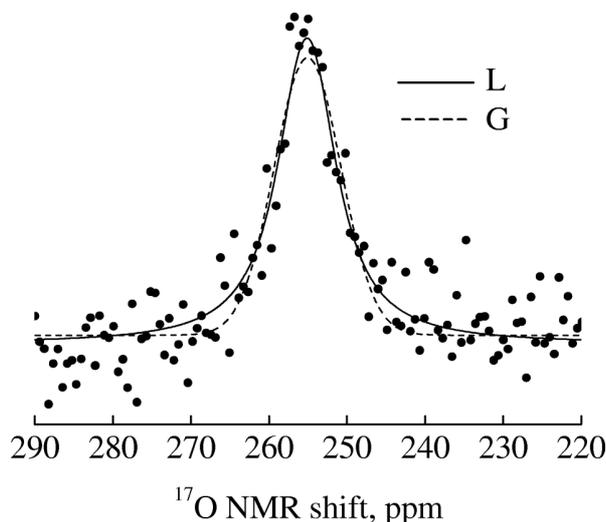


Fig. 5. ^{17}O NMR signal of CyPy·TCA complex in solution (1 M in AN, at 293 K). The experimental contour (points) was approximated by Lorentzian (L) and Gaussian (G) shapes (values of correlation coefficient R^2 are 0.84 and 0.82, respectively) giving the average value of $\Delta\nu_{1/2} = 336$ Hz.

of the ^{17}O NMR signal of carboxylic oxygen and τ_c from $\text{C}_4\text{-H}$ vector rotation that characterize the tumbling of PyO-acid complexes. And now we have to handle an inverse task: to evaluate τ_c having experimentally measured $\Delta\nu_{1/2}$ and taking the 'omphalous' value of 7.5–9.2 MHz interval, i. e. $\chi_{\text{eff}} \approx 8$ MHz. The $\Delta\nu_{1/2}$ of the ^{17}O NMR signal of $-\text{COOH}$ oxygen in CyPy·TCA complex has been evaluated using nonlinear least squares curve fitting (Fig. 5). Then the estimated average value $\Delta\nu_{1/2} = 336$ Hz is inserted into (2) and $(\tau_c)_{\text{HB}} = 17$ ps is calculated. Thus, the

time scale of tumbling of CyPy·TCA seems to be in the range of tens of picoseconds. Furthermore, if one assumes that the relative partition of contributions of various relaxation mechanisms in 'free' and H-bonded CyPy is the same, the rate of tumbling of 'free' CyPy molecule can be evaluated using a simple relation for $-\text{CN}$ carbon $(T_1)_{\text{free}}/(T_1)_{\text{HB}} \approx (\tau_c)_{\text{HB}}/(\tau_c)_{\text{free}}$. This leads to $(\tau_c)_{\text{free}} = 6$ ps that points to an anisotropic character of CyPy reorientations.

Summarizing the data on micro dynamics, we can state that the rotational diffusion even of 'free' CyPy molecules is anisotropic (viz., 3 ps for rotation and 6 ps for tumbling). If we compare with PyO, the values of the rotational correlation time of PyO molecules in AN solution were practically the same for all carbons. That means its rotational diffusion can be considered as isotropic despite a large dipole moment (4.2 D, [23]). It looks like the steric factor is more important – a 'prolongation' of Py molecule by $-\text{C}\equiv\text{N}$ group substitution makes its motion anisotropic. The formation of CyPy·TCA complex causes a general slowdown of the overall rotational motion (7 ps for rotation and 17 ps for tumbling, respectively) with a very slight increase in its anisotropy. Note that the micro dynamical picture of the systems investigated here considerably differs from e. g. Py-phenol complex [17], where much stronger increase (in one order) of τ_c due to the hydrogen bond formation has been found.

Acknowledgements

Support of the Alexander von Humboldt Foundation (Germany) is kindly acknowledged. One of us (V. B.) gratefully acknowledges the hospitality of the Slovenian NMR Centre and the National Institute of Chemistry of Slovenia. We are grateful to Prof. Dušan Hadži for discussions, to Mr Aleksandar Gacesa for his valuable contribution to the NMR experiments, and to Mrs Silva Zagorc for crystal growing and other technical assistance.

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**CIANOPIRIDINO VANDENILINIO RYŠIO KOMPLEKSO SU TRICHLORACTO RŪGŠTIMI
DINAMIKOS IR PROTONO PERNAŠOS TYRIMAI CP / MAS, ¹³C IR ¹⁷O BMR METODAIS**V. Balevičius^a, H. Fuess^b^a *Vilniaus universitetas, Vilnius, Lietuva*^b *Darmštato technikos universitetas, Darmštatas, Vokietija***Santrauka**

Vandenilinio ryšio tarp cianopiridino (CyPy) ir trichloracto rūgšties (TCR) molekulių ypatumai ištirti taikant CP / MAS (cross-polarization / magic angle spinning), ¹³C ir ¹⁷O BMR metodus. ¹³C CP / MAS duomenys patvirtina neutronų ir Röntgen'o spindulių difrakcijos išvadas, kad kristalinėje fazėje susidaro CyPy-TCR kompleksai, kuriuose TCR protonas yra visiškai perneštas link CyPy azoto atomo. Tirpale pasireiškia sudėtingi pusiausvirieji vyksmai, kuriuose konkuruoja visiškoji (VPP) ir dalinė protono pernaša (DPP) bei TCR molekulių dimerizavimasis. Pastebėta tų vyksmų įtaka ¹³C BMR signalų poslinkiams ir suformuluotas eks-

perimentinis DPP virsmo į VPP aptikimo kriterijus. Išmatavus ¹³C ir ¹⁷O BMR relaksacijų trukmes bei NOE (nuclear Overhauser effect) faktorius, apskaičiuoti nesurištųjų ir asocijuotųjų CyPy molekulių sukamojo judesio dinamikos parametrai. Parodyta, kad net ir laisvųjų CyPy molekulių sukimasis yra anizotropiškas, kuris 293 K temperatūroje apibūdinamas atitinkamai 3 ps molekulių sukimosi aplink "ilgąją" ašį ir 7 ps pačios ašies persiorientavimo koreliacijų trukmėmis. Susidarius vandeniliniam ryšiui, molekulių sukimasis sulėtėja, bet anizotropiškumas pakinta nežymiai (koreliacijų trukmės 7 ir 17 ps). Rezultatai palyginti su analogiškais piridino N oksido tyrimų duomenimis.