

# RESUME AND ABSTRACT

## 1) Name and surname

Piotr Bernatowicz

## 2) University degrees:

- master of chemistry, Department of Chemistry, the University of Warsaw, Warsaw, 1995
- doctor of philosophy in chemical sciences, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, 2001

title of the thesis:

„Cross-correlations of nuclear quadrupolar interactions in the studies on molecular structure and dynamics in liquids.”

supervisor: dr hab. Sławomir Szymański

The thesis was awarded the Prize of the Prime Minister of Poland.

## 3) Employment in scientific institutions:

- 1995-1996: apprentice in the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland, as an assistant
- 1996-2001: Ph.D. studies in the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland (1998: 6 months DAAD scholarship at the University of Bayreuth, Germany)
- 2002-2004: postdoctoral position at the University of Stockholm, Stockholm, Sweden
- 2004: since February 2004 to June 2004 assistant in the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland
- 2004-2006: assistant professor in the Institute of Biochemistry and Biophysics, Polish Academy of Sciences, Warsaw, Poland.
- since 2006: assistant professor in the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (2006-2007: Humboldt Foundation scholarship; first part at the Department of Physics at the University of Dortmund, second part at the Department of Chemistry at the University of York)

## 4) The scientific achievement conforming to art. 16 sect. 2 of the act from 14 March 2003 concerning the scientific degrees, scientific titles and titles and degrees in arts (Journal of Laws No. 65, pos. 595 with changes):

### a) the title of scientific/artistic achievement,

„Nuclear magnetic resonance methods in the investigations of molecular dynamics - disentanglement of molecular tumbling and ultrafast local motions.”

**b) (author(s), title/titles of publications, year, publisher),**

1. Bernatowicz P.\*, Kowalewski J., Szymański S., Nuclear spin relaxation in nonrigid molecules: Discrete multisite local dynamics combined with anisotropic molecular reorientation, *J. Chem. Phys.*, 124, art. no. 024108 (2006), IF=3.166

I can estimate my contribution to this article to be 70-75%. I derived the mathematical formalism and wrote the main part of the manuscript, except the chapter discussing the special cases of the dynamics.

2. Bernatowicz P., Kowalewski J.\*, Sandström D., *NMR relaxation study of the protonated form of 1,8-bis(dimethylamino)naphthalene in isotropic solution: anisotropic motion outside of extreme narrowing and ultrafast proton transfer*, *J. Phys. Chem. A*, **109**, 57 (2005), IF=2.898

I can estimate my contribution to this article to be 80-85%. I initiated these investigations, performed the synthesis of the isotopically enriched model compound and carried out 95% of NMR measurements; I prepared the software to numerical analysis of the experimental data and wrote a major part of the manuscript (80%).

3. Bernatowicz P.\*, Kowalewski J., *Carbon-13 NMR relaxation study of 1,8-bis(dimethylamino)naphthalene in isotropic solution*, *J. Phys. Chem. A*, **112**, 4711 (2008), IF=2.871

I can estimate my contribution to this article to be 90%. I initiated these investigations, I performed the NMR measurements (100%), I prepared the software to numerical analysis and wrote a large part of the manuscript (90%).

4. Bernatowicz P.\*, Ruszczyńska-Bartnik K., Ejchart A., Dodziuk H., Kaczorowska E., Ueda H., *Carbon-13 NMR Relaxation Study of the Internal Dynamics in Cyclodextrins in Isotropic Solution*, *J. Phys. Chem. B*, **114**, 59 (2010), IF=3.603

I can estimate my contribution to this article to be 65%. I designed the methodology of the investigations (50%), performed 33% of the relevant NMR measurements and prepared the software to numerical analysis (100%); I interpreted the results (80%) and wrote the manuscript (80%).

5. Bernatowicz P., *A Simple One-Dimensional Method of Chemical Shift Anisotropy Determination Under MAS Conditions*, *J. Magn. Reson.*, **207**, 348 (2010), IF=2.333

6. Bernatowicz P., *Determination of the Rotational Diffusion Tensor of Porphycene by <sup>13</sup>C and <sup>1</sup>H Spin Relaxation Methods*, *J. Phys. Chem. A*, **115**, 8604 (2011), IF=2.946

7. Bernatowicz P., *Accurate determination of ultrafast proton transfer rate in porphycene by nuclear spin relaxation*, *Phys. Chem. Chem. Phys.*, **xxx**, xxx (2013), IF=3.573, DOI: 10.1039/C3CP50963J

**c) description of scientific/artistic aim of the work and achieved results, along with the discussion of their potential applications.**

Nuclear magnetic resonance (NMR) is a versatile tool widely exploited in the investigations of molecular dynamics. The slow and moderately fast processes (rate constants up to  $10^5 - 10^6 \text{ s}^{-1}$ ) can be investigated by numerical analysis of spectral lineshapes or with EXSY experiments. The fast processes with rate constants in the range  $10^6 - 10^9 \text{ s}^{-1}$  can cause complete motional averaging of the spectra. At a high resolution level, they can be studied by measuring the nuclear spin relaxation rates in rotating frame. At the magnetic field strengths typical for modern high resolution NMR spectrometers, laboratory frame measurements of nuclear spin relaxation rates are effective in the investigations of still faster molecular processes, with rate constants exceeding  $10^9 \text{ s}^{-1}$ . This is feasible if the only source of the spin relaxation is the overall molecular tumbling, which for small molecules in nonviscous liquids occurs on such a time scale. The problem is more complicated if local dynamics (e.g., intramolecular proton jumps, methyl group reorientation, torsional motion of a ring etc.) of a similar time scale to that of the tumbling is of interest. Then both types of dynamics can have comparable impact on the NMR relaxation observables. The aim of this work was the elaboration of an efficient method of the investigations of such difficult cases.

Article [1] contains derivation of the mathematical formalism which links parameters of the molecular structure and dynamics to the so-called spectral densities, which are quantities characterizing stochastic molecular motions as functions of frequency. In measurements of NMR observables such as longitudinal relaxation rate, transverse relaxation rate, nuclear Overhauser effect etc., linear combinations of the values at known frequencies of these functions can be determined. Several models describing spectral densities in the systems involving local dynamics had been published previously, but all of them have a rather low level of generality. This dramatically limited the scope of applicability of the above mentioned NMR methods to molecules of high (axial) or extremely high (spherical) symmetry only. In addition, the earlier treatments involved drastic simplifications of the description of the spin interactions underlying the relaxation phenomena, assuming their axial symmetry. This precluded accurate investigations of molecular dynamics, even for models with axial or spherical symmetry. In particular, these drawbacks can manifest themselves in the cases where e.g. the ubiquitous chemical shielding anisotropy or (less common) electric interaction of the nuclear quadrupoles, are significant relaxation mechanisms. The two latter mechanisms are of axial symmetry only in very special cases i.e. when the relevant atom lies on a threefold (or higher) symmetry axis of the molecule. The formalism derived in article [1] is not hampered by such restrictions. It can be applied to molecules of any shape, if the discrete local

dynamics involved (the continuous case is considered in [4]) is statistically uncorrelated with global tumbling, i.e. when local motions do not alter the rotational diffusion tensor of the molecule. The present formalism succeeds, therefore, in a substantial extension of the scope of applicability of the spin relaxation techniques in the studies on the molecular dynamics in liquids. The general equations derived in article [1] are quite complicated. Therefore, the second part of this paper addresses some commonly encountered cases where substantial simplifications are possible. These include two-site exchange and multi-site exchange with equal populations (e.g. methyl group rotation). The case of proton jumps between two acceptors of hydrogen bond (a case of two-site exchange with equal populations) was considered in detail in articles [2] and [7]).

Articles [2] and [3] contain description of application of the above-mentioned theory to the investigations of the so-called proton sponge (see Fig. 1), denoted further as DMAN (from 1,8-bis(DiMethylAmino)Naphthalene). This molecule is an extremely strong base which undergoes protonation in reaction with acids. The absorbed proton is trapped inside a symmetric double-well potential between two nitrogen atoms. The aim of article [2] was the investigation of the dynamics of proton jumping in the

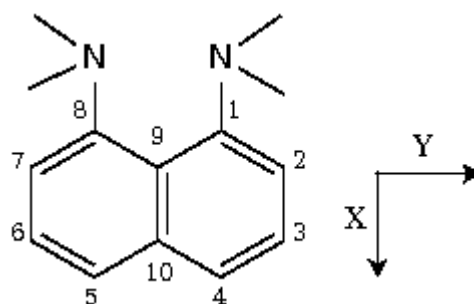


Figure 1: 1,8-bis(dimethylamino) naphthalene (DMAN) and principal axes of its rotational diffusion tensor

N...H...N bridge between the minima of the potential. First, the principal components of the rotational diffusion tensor of the protonated DMAN at temperatures between 213 and 303 K were determined. To this end, the  $^{13}\text{C}$  longitudinal relaxation and  $^{13}\text{C}\{^1\text{H}\}$  NOE effect in the naphthalene skeleton were measured at several magnetic fields and analyzed numerically. Directions of the principal axes of this tensor were fortunately predetermined by effective (average)  $C_{2v}$  symmetry of the molecule. Their arrangement is shown in Fig. 1. In the next step, the longitudinal relaxation rates of  $^{15}\text{N}$  nuclei and  $^{15}\text{N}\{^1\text{H}\}$  NOE effect were analyzed numerically, with the conclusion that in the whole temperature range of interest the bridging proton jumps are faster (by at least 2 orders of magnitude) than the maximum rate constant of the molecular tumbling, which was estimated to be about  $10^{10} \text{ s}^{-1}$ . Accurate determination of the jump rate constant for such a fast process was not possible. The principal components of the rotational diffusion tensor for unprotonated DMAN were determined in article [3] in similar temperature range as it was accomplished for  $\text{DMANH}^+$ . The activation energies were determined from Arrhenius plots of the individual components of the rotational diffusion tensors of DMAN and  $\text{DMANH}^+$ . It comes out that the protonation significantly affects reorientation about the Y and Z axes, while the activation energy about axis X remains practically unchanged. The ultimate conclusion was that the counterion, which in this particular

case was the  $\text{NO}_3^-$  anion, forms an ion pair with  $\text{DMANH}^+$  and is located on the  $C_2$  symmetry axis of  $\text{DMANH}^+$  near the N...H...N bridge. Such an ion pair is stable on the timescale of molecular reorientation.

Article [4] is devoted to relaxation investigations in a series of 7 cyclodextrins. The smallest of them,  $\alpha$  (see Fig. 2), is a macrocyclic molecule comprising 6 glucopyranosic rings, linked to one another by O-glycosidic bonds. The largest investigated

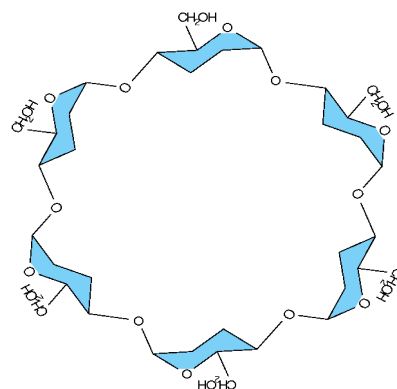


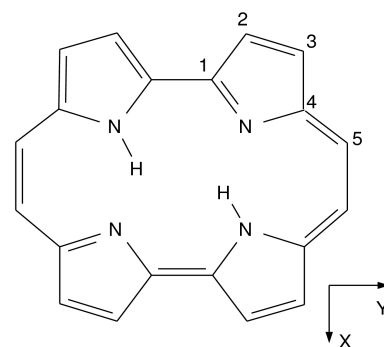
Figure 2: Cyclodextrin  $\alpha$

one,  $\eta$ , is an analogue of  $\alpha$  but its cyclic structure includes 12 rings of glucose. The mechanism of the internal dynamics considered in article [4] comprises large-amplitude torsional vibrations of the individual glucopyranosic rings about axes going through their glycosidic oxygen atoms, O1 and O4. Under this assumption, a good reproduction of relaxation observables was obtained. In small cyclodextrins,  $\alpha$ – $\gamma$ , these vibrations are faster than molecular reorientation, while in the large rings,  $\delta$ – $\eta$ , they are slower. The analysis of spin relaxation allows also for the estimation of both the average angles between the plane of the macrocycle and planes of the individual glucopyranosic rings and the amplitudes of the torsional vibrations of these rings about the O1-O4 axes. The determined values of these quantities for cyclodextrins  $\alpha$ – $\gamma$  are in good agreement with crystallographical measurements and with the results of molecular dynamics calculations reported in the literature. Similar structural data for the larger macrocycles,  $\delta$ – $\eta$ , delivered by methods other than NMR, are, unfortunately, not available in the literature. The determined components of the rotational diffusion tensors reveals an anomaly for cyclodextrin  $\beta$ , in comparison to  $\alpha$  and  $\gamma$ . The microscopic origin of this anomaly is still not clear, but it is well known that there occurs a similar anomaly in the solubility in water: for species  $\beta$  it is roughly an by an order of magnitude lower than for  $\alpha$  and  $\gamma$ . It is remarkable that the assumed mechanism of the internal dynamic in cyclodextrins is continuous, while in the formal treatment of article [1] discrete jumps are assumed. It has come out, however, that the continuous dynamic can in practice be approximated in terms of discrete jumps between a large number of hypothetical conformers. The fact that the latter approach has proven efficient for such complicated models as the cyclodextrins has practical consequences: It affords one to conclude that the limitations of the formalism derived in article [1] resulting from the assumed discreteness of the dynamic process can be *de facto* bypassed.

Article [5] presents a novel method of determination of principal components of chemical

shielding anisotropy tensors, alternative to the widespread 2D-PASS protocol. These components, expressed in terms of the so-called relaxation interaction strengths, are important parameters in the equations linking molecular dynamics to spectral densities (the general form of such equations was reported in article [1]). An independent experimental determination of such parameters is crucial for a precise interpretation of the relaxation data. The proposed method consists of a simultaneous numerical analysis of several MAS spectra acquired at various, suitably chosen, spinning rates of the sample. This method was successfully exploited in article [5] to determine chemical shielding anisotropy tensors of  $^{13}\text{C}$  nuclei in porphycene, which were further used in the investigations of the rotational diffusion of this molecule, described in article [6]. The developed method is less demanding with respect to spectrometer hardware than the 2D-PASS one since, in contrast to the latter, the exploited pulse sequence is not rotor-synchronized. The presented method also requires lower number of acquired spectra and less scans per spectrum than a typical 2D-PASS experiment.

In article [6] the  $^{13}\text{C}$  relaxation observables in porphycene (see Fig. 3) were analyzed in order to determine the rotational diffusion tensor concerned. It turned out that the reorientation of this molecule about axis Z is significantly faster than about the remaining axes. This result is quite surprising, since the magnitude of component Z of the moment-of-inertia tensor of this molecule is the biggest one, so that it could be expected that reorientation about axis Z would be slower than about the X and Y axes. Also the domination by factor 1.56 of the rotational diffusion constant around axis X over that about Y does not reflect the relationship between the corresponding components of the moment-of-inertia tensor, which are almost equal to each other. This leads to conclusion that the moment-of-inertia tensor cannot be used for the prediction of molecular reorientations in solutions, even as a rough approximation. In article [6], the nontrivial problem of vibrational correction to a one-bond  $^{13}\text{C}$ - $^1\text{H}$  dipole-dipole coupling within the so-called extreme narrowing regime was addressed. Previously, in article [2], the vibrational correction could be determined outside the extreme narrowing limit; in somewhat arbitrary way it could then be extrapolated to the extreme narrowing regime. For porphycene, however, the molecular reorientation at the experimentally accessible temperatures was so fast that the relevant dynamics in the extreme narrowing regime had to be confronted with. Therefore, an alternative approach was exploited, involving an augmentation of the  $^{13}\text{C}$  with the pertinent  $^1\text{H}$  relaxation data, with the final numerical analysis performed on the combined data set. This allowed for the determination of the



*Figure 3: Porphycene and principal axes of its rotational diffusion tensor*

one-bond  $^1\text{H}$ - $^{13}\text{C}$  vibrational correction, whose magnitude turned out to be very similar to that observed earlier in  $\text{DMANH}^+$ .

The investigations of the  $^{15}\text{N}$ -labeled porphycene are described in article [7]. Using the rotational diffusion tensor components derived earlier for the unlabeled compound as reported in article [6], numerical analysis of the  $^{15}\text{N}$  relaxation observables yielded the rate of proton jumps in the N...H...N bridges. The obtained value of  $(1.0 \pm 0.57) \times 10^{12} \text{ s}^{-1}$  agrees well with that of  $(5.8 \pm 0.3) \times 10^{11} \text{ s}^{-1}$  determined in liquids by the group of professor Waluk using optical spectroscopy methods. Both the above values significantly differ from the value  $4.9 \times 10^7 \text{ s}^{-1}$  which was determined by the group of professor Limbach for the solid porphycene. Article [7] describes the first case of NMR investigations leading to the quantitative determination of rate constant of a ultrafast local dynamics in a molecule undergoing Brownian motions in isotropic liquid.

Conclusions: Mathematical formalism allowing for accurate investigations of the local molecular dynamics in liquids by methods of nuclear spin relaxation, free of most of the limitations of the earlier approaches, was derived. The experimental methodology based on this formalism was tested and elaborated on a few molecular models. It was shown that NMR is a method which can be used for accurate investigations of the local dynamic processes, both intra- and intermolecular, even if the associated overall molecular tumbling is of a similar rate. The elaborated method allows for the determination of the parameters of the overall molecular tumbling, too.

## 5) Miscellaneous scientific achievements

After accomplishing my Ph.D. thesis I have been a coauthor of 17 scientific articles, which have not been included into the present work:

1. Dinnebier R. E., Bernatowicz P., Helluy X., Sebald A., Wunschel M., Fitch A., van Smaalen S., *Structure of compounds  $E(\text{SnMe}_3)_4$  ( $E=\text{Si}, \text{Ge}$ ) as seen by high-resolution X-ray powder and solid-state NMR*, Acta Crystallogr. B, **58**, 52 (2002), IF=2.026
2. Bernatowicz P., Szymański S., *Wave properties of a methyl group under ambient conditions*, Phys. Rev. Lett., **89**, art. no. 023004 (2002), IF=7.323
3. Kamińska-Trela K., Bernatowicz P., Lüttke W., Machinek R., Traetteberg M., *One-bond  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constants in alkyl-substituted cyclopropenes: experimental and theoretical studies*, Magn. Reson. Chem., **40**, 640 (2002), IF=0.994
4. Bernatowicz P., Kruk D., Kowalewski J., Werbelow L.,  *$^{13}\text{C}$  NMR lineshapes for the  $(\text{CHH})$ - $^{13}\text{C}$ - $^2\text{H}$ - $^2\text{H}'$  isotopomeric spin grouping*, ChemPhysChem, **3**, 933 (2002), IF=3.862
5. Jackowski K., Bernatowicz P., Wielogórska E., *Intermolecular interactions of aliphatic nitriles in*

- aprotic solvents studied by  $^{13}\text{C}$  and  $^{14}\text{N}$  NMR chemical shifts*, Z. Phys. Chem., **216**, 1401 (2002), IF=0.854
6. Wunschel M., Dinnebier R. E., Carlson S., Bernatowicz P., van Smaalen S., *Influence of the molecular structures on the high-pressure and low-temperature phase transitions of plastic crystals*, Acta Crystallogr. B, **59**, 60 (2003), IF=3.643
7. Bernatowicz P., Szymański S., *Magnetic equivalence of terminal nuclei in the azide anion broken by nuclear spin relaxation*, Mol. Phys., **101**, 353 (2003), IF=1.591
8. Czernski I., Bernatowicz P., Jaźwiński J., Szymański S., *Nonclassical effects in liquid-phase nuclear magnetic resonance spectra of 9-methyltritycene derivatives*, J. Chem. Phys., **118**, 7157 (2003), IF=2.95
9. Bernatowicz P., Szymański S., *NMR lineshape equations for hindered methyl group: a comparison of the semi-classical and quantum mechanical models*, J. Magn. Reson., **164**, 60 (2003), IF=2.084
10. Bernatowicz P., Czernski I., Jaźwiński J., Szymański S., *Carr-Purcell echo spectra in the studies of lineshape effects. Nonclassical hindered rotation of methyl groups in 1,2,3,4-tetrachloro-9,10-dimethyltritycene*, J. Magn. Reson., **169**, 284 (2004), IF=2.461
11. Bernatowicz P., Kowalewski J., Kruk D., Werbelow L. G.,  *$^{13}\text{C}$  NMR line shapes in the study of dynamics of perdeuterated methyl groups*, J. Phys. Chem. A, **108**, 9018 (2004), IF=2.639
12. Szymański S., Bernatowicz P., *The Symmerization Postulate of Quantum Mechanics in NMR Spectra*, Ann. Rep. on NMR Spectr., **54**, 1 (2005), IF=1.778
13. Bernatowicz P., Nowakowski M., Dodziuk H., Ejchart A., *Determination of association constants at moderately fast chemical exchange: Complexation of camphor enantiomers by alpha-cyclodextrin*, J. Magn. Reson., **181**, 304 (2006), IF=2.076
14. Ghalebani L., Bernatowicz P., Aski S. N., Kowalewski J., *Cross-correlated and conventional dipolar carbon-13 relaxation in methylene groups in small, symmetric molecules*, Concepts Magn. Reson. A, **30**, 100 (2007), IF=0.812
15. Bugaj M., Baran P. A., Bernatowicz P., Brożek P., Kamieńska-Trela K., Krówczyński A., Kamieński B., *Structural studies on aryl-substituted enaminketones and their thio analogues. Part I. Analysis of high-resolution  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and  $^{13}\text{C}$  CP MAS spectra combined with GIAO-DFT calculations*, Magn. Reson. Chem., **47**, 830-842 (2009), IF=1.612
16. Gregorowicz J., Bernatowicz P., *Phase behaviour of L-lactic acid based polymers of low molecular weight in supercritical carbon dioxide at high pressures*, J. Supercrit. Fluids, **51**, 270-277 (2009), IF=2.639
17. Zep A., Aya S., Aihara K., Ema K., Pocięcha D., Madrak K., Bernatowicz P., Takezoe H.,



Gorecka E., *Multiple nematic phases observed in chiral mesogenic dimers*, J. Mater. Chem. C, **1**, 46 (2013), IF=5.968

In 2006 I was awarded a scholarship by the Alexander von Humboldt Foundation.

Warsaw, 6 May 2013

Piotr Bematoriusz