



**Oponentský posudek disertační práce**

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**Supervisor:** doc. Mgr. Robert Vícha, Ph.D.  
**Consultant:** Ing. Zdeňka Prucková, Ph.D.  
**Title:** Synthesis of Rotaxane Structures with Multitopic Ligands  
Syntéza rotaxanových struktur s vícevazebnými ligandy

The above-mentioned doctoral thesis represents a representative cross-section of the issues addressed in the group of doc. Robert Vícha at TBU Zlín. The dissertation deals with the synthesis and research of the properties of new types of rotaxanes (wheel-on-axle) based on the chemistry of cucurbiturils or cyclodextrins. The gradual development of three different generations of linear molecules (axles) led to the systems enabling the targeted threading of the aforementioned macrocycles onto the central axis of the rotaxane, forming supramolecular complexes with interesting properties. Very impressive results were brought by the study of the behaviour of these rotaxanes and the possibility of targeted influence of the threading or dethreading process by external circumstances, such as the addition of another macrocycle or the use of a competitive linear molecule to decompose the supramolecular complex.

The Thesis is written in good English (and has the usual formal structure. The first part presents a theoretical introduction describing mechanically interlocked systems and molecular machines with a special emphasis on the current state of the art in the field of rotaxanes (40 pages).

This is followed by the Experimental section, where the syntheses and characteristics of the prepared compounds are described on 27 pages. In this context, it should be noted that the synthesis was not the basis of this work and served only to obtain the relevant rotaxane axes. Therefore, this chapter is relatively short.

The main part of the Thesis is a discussion of the results (> 60 pages), where the functioning of supramolecular systems depending on the individual generations of the respective axles is described in details. Considering how complex the issue is, the behaviour of supramolecular complexes is described very clearly and comprehensibly. It is obvious that the author has devoted maximum effort to clarifying the behaviour of the corresponding rotaxanes, using several complementary approaches including NMR titrations, kinetic experiments, HRMS, X-ray or ITC.

All parts of the Thesis are of high scientific quality, the high level of elaboration is consistent throughout the thesis. The conclusions are supported by thorough experimental work, all input assumptions are based on a good knowledge of the state-of-the-art in the given field. Part of the results achieved in this dissertation has already been published in two prestigious international high-impact journals (JOC, Chem. Sci.). This indicates the high quality and relevance of this research and demonstrates the importance of the topic within basic research in the field of supramolecular chemistry.

Regarding the dissertation itself, I have the following comments and topics for discussion:

- p. 33: I appreciate the effort to colour-code relatively complex schemes and structures, but in this case it's a bit counterproductive - the strange blue colour makes the situation more difficult. Fortunately, I know the image, otherwise it would be almost unreadable.



- Across the experimental part: I am aware that  $\text{cm}^3$  is an SI unit, but I don't know anyone in organic chemistry who would add  $30 \text{ cm}^3$  of water, because we all use the "old good" millilitres. In this context, I find it strange that you don't stick to the correct organic nomenclature (which, by the way, seems much more important to me). Names like 1,4-diaminobutane or 1,6-diaminohexane (throughout the text) are incorrect and not allowed. The presence of only amine groups in the parent structure can only be described using a suffix, not a prefix! So, the correct names are: butan-1,4-diamine or hexan-1,6-diamine – see Nomenclature of Organic Chemistry. IUPAC Recommendations and Preferred Names 2013, ISBN 978-0-85404-182-4 ([Blue Book](#)).
- p. 86: The reported association constant for hexane-1,6-diammonium@CB6 complex is  $2.9 \times 10^8 \text{ M}^{-1}$  (50 mM NaCl solution, ITC) while you obtained  $K = 7.9 \times 10^9 \text{ M}^{-1}$  in 2.5 mM NaCl, ITC). This represents a 27x larger value of the constant. Do you have any explanation for such a significant difference?
- In connection with the previous point. When you measured association constants (e.g. Table 6 or Table 7) using the competitive method, you take as a basis the values of constants known from the literature. Is it guaranteed that the competitive experiments were carried out under identical conditions as in the literature? Otherwise, there can obviously be a deviation of several orders of magnitude?!
- Still in connection with the previous text. Table 7 (Association constants determined by competitive experiments). Does using different reference compounds (AMMI and PXD) for the rotaxane and its axis make any sense? How reliable is this data?
- p. 93, Figure 46: The text says L5 + 1.5 equiv. of CB6, the image description says 1:1 mixture. Which is correct?
- Figure 46: The spectrum of the mixture L5 + CB6 measured after 14 days at 303 K, in my opinion, shows the formation of some other species. Note the signals around 1.1-1.2 ppm. This is not mentioned in the text, can you please comment on it?
- p. 138, Table 8: While the  $\Delta G$  values for the complexes of ligand **32** with CB6 and CB8 are practically the same, their enthalpic and entropic terms are significantly different. Do you have any explanation?

Despite the above comments, I have to emphasize that the author has done a lot of work, leading to a number of interesting results. Hence, in conclusion, it can be stated that the student has demonstrated appropriate creative abilities in the given direction of research and the submitted work meets the standard requirements for dissertations in the given field.

For the above reasons, **I recommend** to accept the submitted dissertation of Ing. Aneta Závodná for defence as a basis for obtaining the scientific degree of Ph.D.

In Prague  
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