UNIVERSITY OF CHEMISTRY AND TECHNOLOGY, PRAGUE
Faculty of Chemical Technology
Department of Organic Chemistry

Expert opinion on Ph.D. thesis entitled: "The synthesis of π-electron systems suitable for transfer and retention of charges"

The submitted Ph.D. thesis is focused on the synthesis of helicene-based π-conjugated molecules. The presented work successfully develops the area of the supervisor's long-term research interest in the chemistry of helicenes and their electron transport properties. The field of organic semiconductors is a hot topic in current material chemistry. As per usual, the dissertation is divided into several parts (*Introduction*, *Objectives*, *Results and Discussion*, *Conclusion*, *Experimental section*, *Abbreviations*, *Literature*, *Appendix A*). The *Introduction section* (35 pages) focuses on synthetic approaches to substituted helicenes. Moreover, the short introduction (17 pages) describes break junction techniques and the electron transport properties of helicenes. The *Results and Discussion* describes the synthesis of target helicenes by [2+2+2] cycloisomerization. A stepwise procedure was used to synthesize building blocks that are typically cyclized by flow reactor chemistry and, in some cases, by microwave chemistry. The introduction of S-spacers was achieved by nucleophilic aromatic substitution at a high temperature. The *Results and Discussion* section ended with a description of the experimental setup for break junction experiments, as well as a description of the results.

Formally, the doctoral thesis is very well organized. The presented results in the form of tables, diagrams, pictures, and graphs are arranged according to the standards of scientific publications. The obtained results and the work procedure are logically arranged. During his work, the student proved that he is capable of systematic work and can logically solve problems. The presented results show that Mgr. Jindřich Nejedlý is not only familiar with the issue of helicene synthesis, but he also masters skills that are necessary in the field of multidisciplinary projects. Examples include the syntheses using microwave chemistry and flow reactors and the use of advanced NMR techniques to determine the structures of the prepared substances. It is also worth mentioning his participation in conductivity measurements.

As mentioned in the introductory part of the report, the dissertation is of a very high quality. Nevertheless, I found some parts to be confusing. An example is the retrosynthetic analysis of oxahelicene **89** (page 39). I do not understand why helicene, which was not synthesized, was used in the retrosynthetic discussion. It is not clear from Table 4 (page 54) what the reaction times for the first and second reaction steps are. The experimental part is arranged according to the standards typical for professional texts. The description of the experiments is clear, and I have no doubt about the reproducibility of the performed experiments. In this context, it is a pity that the author omitted the description of measured spectra for known substances and was satisfied only with the statement that the spectra are consistent with the literature. In this case, it is possible to guess the spectra that were measured. It is also a pity that there are no copies of ^{1}H (^{13}C) NMR spectra of the selected helicenes in the appendix to the dissertation, so that the reader can get an idea of the purity of the prepared substances.

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The thesis contains minimal grammatical and typographical errors. Here are some examples:
Literature: Some references have incorrect journal abbreviations (ref. 20, 51) or an article title (ref. 65).
Page 96: Substance **95** lacks a description of appearance. The same applies to compound **97** (page 97).
Page 133, compound **153**: "1H NMR" should be "^{1}H NMR"
Page 133, compound **153**: "13C NMR" should be "^{13}C NMR"

The following questions arose while reading this doctoral thesis:
1. Why was 1.55 equiv. of BuLi used for the preparation of compound **97** (Scheme 25)? Is this amount of BuLi supported by the optimization study? In other words, I wonder what happens when 1.51 equiv. or 1.59 equiv. BuLi is used.
2. Based on what considerations were helicenes chosen for the conductivity measurement? Was the choice of target substances influenced by the synthetic availability of helicenes or were quantum-chemical calculations performed for the design of the studied structures?
3. Is it possible to deduce what the effect of helicene structure or S-spacer placement on conductivity of tested helicenes **134**, **136**, **139**, **131**, **168**, **146**, **143**, **145**, and **148**? Particularly, substances **131** and **168** do not fit into the measured series and, therefore, it will be very difficult to correlate the obtained results. Especially in helicene **168**, where the presence of heteroatoms and substituents that may affect the resulting conductivity should be considered.
4. Why were only oxahelicenes considered for conductivity measurements? It is conceivable that analogous thiahelicenes would have different electron transport properties.

Let me conclude the report by saying that the presented Ph.D. thesis is a collection of high-quality original results. The aims of the thesis were reached, and Mgr Jindřich Nejedlý published 4 papers (two as the first author). Therefore, I recommend that this Ph.D. thesis is accepted as the basis for defending the Ph.D. academic degree.

In Prague 2. 11. 2020

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