UNIWERSYTET IM. ADAMA MICKIEWICZA W POZNANIU
Wydział Chemii, Zakład Syntezy Nanostruktur Funkcjonalnych
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REPORT ON THE DISSERTATION ENTITLED "APPLICATIONS OF α-α COUPLING AND α-α BRIDGING IN THE SYNTHESIS OF ELECTRON-DEFICIENT OLIGOPYRROLES"

The basis for issuing the opinion on the doctoral dissertation of Liliia Moshniaha is the letter of Prof. Dr. Hab. Marcin Stępień, Chairman of the Scientific Council of the Chemical Sciences Discipline of the University of Wrocław on March 23, 2022 (DWCh.412.3.2022.AK)

A dissertation submitted by Liliia Moshniaha *(hereafter referred to as the Candidate)* consists a basis for awarding the Doctoral degree. The thesis has been conducted under the supervision of Prof. Marcin Stępień at the Faculty of Chemistry, University of Wroclaw, and it correlates well with the research activities successfully conducted in this team. The report, which I had a pleasure to provide, will be divided into separate sections describing various aspects of the thesis.

1) Thesis content and contribution to the field

The *Thesis* consists of 192 pages, and it has been written using a standard layout. It begins with the Contents, followed by the Research Objectives, the list of Abbreviations, the Literature Review, and more technical sections in which Bridged Azacoronenes *via* Electrophilic Condensations with Aldehydes, Synthesis of Bipyrrole derivatives *via* Double C-H Bond Activation are described. List of authors Contributions has been discussed prior to the Conclusions, and Acknowledgements. The thesis ends with the list of Publications and extensive (388 items!!!) list of References.

The literary essay contains a thematically relevant, concise introduction that guides the reader along the topic in a very accessible manner. It also provides the theoretical background necessary to understand the context of the results described in the subsequent parts of the *Thesis*. The subchapter 3.1. includes the description of effective synthetic strategies of PAHs based on efficient ring-formation processes. The procedures allowing the construction of the fundamental ring are generally referred to as *ortho-* and *peri-*annulations. Following subsection illustrates the use of palladium compounds in the synthesis of π-conjugated decorated polycycles. Last subchapter in literature review concerns new azacoronenes and related structures such as hexapyrrolohexazacoronenes – prototype nanographene comprising *peri*-fused pyrrole rings. The described techniques for the synthesis of these compounds can be used to design and generate three-dimensional nanographene oligomers and nanocages with potential applications in materials science and supramolecular chemistry.

Chapter 4 of this *Thesis* describes unprecedented synthesis of the 139-π-electron nanographenoid radical by extending the periphery of a naphthalimide-azacronene hybrid with a metin bridge. The radical was isolated in the form of its σ-dimer, which turned out to have a conformationally constrained bilayer structure in both solid state and in solution. It was observed that under the influence of ultraviolet or Vis light irradiation, a dimer was observed being cleaved from its parent radicals in toluene, but is resistant to thermally induced dissociation. Under neutral conditions, radicals recombine quantitatively into σ-dimer with observable kinetics, yet, are oxidized with a ketone derivative in the presence of atmospheric oxygen. This has been confirmed by the structural and spectroscopic investigations, which have shown that the σ-dimer contains a weak C(sp^3)-C(sp^3) bonding, but it is stabilized against thermal dissociation through a very strong dispersion interaction between the overlapping π surfaces. The obtained results were additionally supported by the DFT calculations that the *Candidate* carried out herself, which clearly illustrates the holistic approach of the *Candidate* to her scientific work.

In this chapter the *Candidate* reports on the initial synthetic attempts towards generation of bridged hexapyrrolylbenzenes through acid-catalyzed condensation between naphthaleneimide-fused precursor with five aldehydes under different reaction conditions (various amounts of the aldehyde, catalyst, and different solvents, as well as temperature variations and reaction time). The *Candidate* therefore turned her attention to the quintuply coupled system, which is easily obtained in high yields by mild oxidation of naphthaleneimide-fused precursor with ferric chloride and synthesized nanosandwich by electrophilic bridging. Unfortunately, this method also turned out to be ineffective. Finally, an efficient condensation was used to reduce the steric mass of the aldehyde reagent. To this end, paraformaldehyde was used which reacted with quintuply coupled system in the presence of 10-camphorsulfonic acid catalyst. Surprisingly, this product was identified as a σ-dimer.

The results of the research presented in Chapter 5 are an excellent example of finalization of the chemical idea, which the *Candidate* included in the application for funding in the framework of the PRELUDIUM project entitled "Double C-H bond activation. A new tool for synthesis of extensively conjugated oligopyrrole materials" awarded by Experts and Reviewers of the Polish National Science Centre. This part of the *Thesis* ilustrates that the tandem cyclization–oxygenation reaction is a commonly used strategy for the synthesis of low-bandgap bipyrrole boomerangs and is applicable to targets with variable donor–acceptor character and increasing curvature of the bipyrrole linkage. The performance of the oxidation step depends on several factors, a broad spectrum of which was studied by the *Candidate*.

Chapter 6 describes detailed contribution of the *Candidate* and co-authors.

Chapter 7 contains the results of the conducted research presented in the form of detailed descriptions of experimental procedures (24 pages). Noteworthy, the Candidate used various analytical techniques such as NMR, UV-Vis and UV-Vis-NIR spectroscopy, HR-MS spectrometry, chromatography, irradiation to perform and analyze all the experiments described in this *Thesis*. Moreover, these techniques are typically used in various scientific settings, which demonstrates the high commitment of the *Candidate* to carry out the research at the highest level.

The *Thesis* ends with conclusions indicating the crucial role of choosing an efficient method for the synthesis of bridged hexa-*peri*-hexabenzocoronenes and hexapyrrolohexaazacoronenes systems.

The excellent reputation of the *Candidate's* supervisor, and the research team in which the work was performed had set the expectation for this *Thesis* at the highest level. And indeed, as expected, the quality of this *Thesis* is not disappointing at any point. The ever-increasing need to search for the tool for synthesis of large π-conjugated heterocycles has made many scientific groups to carry on extensive research in the area, I believe that the scope of work presented in this Thesis is extremely important and useful not only from a purely scientific point-of-view, but also due to the high application potential as functional dyes or the bipyrrole boomerangs characterized of their very high fluorescence quantum yields, the best so far recorded for this family of fluorophores may be usable as circularly polarized luminescence emitters, provided that their helicene-like twist is further stabilized against racemization.

2) Quality of the work

In the dissertation, the *Candidate* has demonstrated a good knowledge and understanding of the basic principles of the nontrivial part of organic chemistry, as evidenced by in-depth discussion. The scientific novelty and effectiveness of the tasks formulated in the dissertation are confirmed by two experimental publications one in one of the most prestigious journals in the field of chemistry, i.e., *Journal of the American Chemical Society* and the second in a very good specialized journal - the *Beilstein Journal of Organic Chemistry*. The *Candidate* is a co-author of a comprehensive review (794 entries), which describes recent developments in the chemistry of PAHs. The article covers literature published between 2016 and 2020, updating the first review of this topic from Chem. Rev. (2017, 117, 3479-3716) announced by Prof. Stępień's group. The quality of the results and their originality is scrupulously evaluated by external reviewers and the editorial board. For this reason, I believe that re-describing and re-evaluating the quality of these data and summarizing them again is unnecessary.

3) Presentation:

The presentation is very good, in particular in view that the *Candidate* is not a native speaker. The quality of figures and graphs used for the schematic representation of the results obtained is very high. Descriptions and the format of the thesis are clear. The experimental data are presented concisely and clearly. There is a good balance between the different parts of the *Thesis*. I believe that even the best and most thoroughly described activities do not illustrate the enormous work, those countless hours spent by the *Candidate* in the laboratory. Therefore, it remains for me to consider the *Candidate* as an extremely experienced organic chemist with a research curiosity and an open mind.

4) Originality

Undoubtedly, an aspect of the scientific novelty contained in this doctoral dissertation is the synthesis and examination of the properties of the heteroaromatic radical obtained by the peripheral expansion of a naphthalimide-fused hexapyrrolohexaazacoronene. This is a beautiful example of combining the supervisor's visionary idea with practical implementation by a PhD student, which resulted in stunning effects of their scientific collaboration.

5) Summary

The *Thesis* contains original and valuable scientific results of development of chemistry of polycyclic heteroaromatics, which is an important contribution to organic and nanographene chemistry. I would like to point out that the research undertaken by the Candidate student concerns the most current issues in one of the most dynamically developing fields of modern science – chemistry of Policyclic Aromatic Hydrocarbons. The thesis represents a great deal of work. The results are well presented, and their interpretation is at the high scientific level. I really appreciate the Candidate expertise in the field of organic and theoretical chemistry. I find the dissertation of Ms. Liliia Moshniaha as conceptually very interesting. The work was properly conducted and reported with due care and competence, and the analysis of the experimental results is insightful.

The exceptional scientific activity of the Candidate deserves to be emphasized. In addition to three publications included in the dissertation, she is the co-author of two other articles in reputable journals (*Chemistry-A European Journal, Journal of Organic Chemistry*). My sincere applause for the *Candidate's* achievements should not really come as a surprise to me, since her doctoral dissertation was carried out under the scientific supervision of Prof. Marcin Stępień, a recognized specialist in organic chemistry, whose unprecedented scientific achievements are highly valued by the world scientific community.

Therefore, I thank the High Scientific Council of the Chemical Sciences Discipline of the University of Wrocław for the honor of being a reviewer of the work under review.

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In view of the above, I believe that the dissertation meets all the requirements and I recommend the Scientific Council of the Discipline of Chemical Sciences at the University of Wrocław to award the candidate the PhD degree. At the same time, due to the high quality of experimental results contained in the doctoral dissertation, innovative ideas, which will certainly affect the development of the studied field, I recommend for its distinction.

Patroniak

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