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The assessment of the PhD Thesis by

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"Development of new syntheses of condensed aromatic compounds"

Reviewer:

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The submitted PhD Thesis by Reinhard Peter Kaiser presents his most important achievements in the field of the synthesis of nonplanar polyaromatic compounds with an embedded 9,9'-spirobifluorene backbone. The author pays attention also to the introduction of various substituents that may control the engineered photophysical properties.

The submitted PhD Thesis presents a modern approach to new materials for envisaged applications to organic electronics and photovoltaics and, accordingly, it follows modern trends of contemporary aromatic chemistry and material science. I really appreciate the results attained demonstrating the applicant's ability to conduct a high-standard research in the perspective field of science. I have no doubt about the validity and originality of the acquired data that are well documented and convincingly presented.

The first part of the Thesis ("Literature Review", 26 pp) covers synthetic approaches to fluorene derivatives. It is comprehensive and well organised. However, the methodologies for the preparation of a 9,9'-spirobifluorene backbone, which is one of the central themes of the Thesis, are omitted (with one exception described in Scheme 32). That's surprising as 9,9'-spirobifluorene unit (the naked one is commercially available) has already been utilised, e.g., in enantioselective catalysis constituting chiral ligands for transition metals. Also the well-established synthetic methodology for the preparation of helically chiral aromatics (helicenes and their derivatives) utilising [2+2+2] alkyne cycloisomerisation is not mentioned even though the author used this concept in his work.

Other comments to this part:

- Scheme 2 and 5 captions: compounds **II** are fluorenones (not fluorenes).
- Scheme 10 caption: the compounds **XVIII** are not only fluorenes but also their derivatives, fluorenones or dibenzo[*b,d*]furanes.
- Scheme 13 caption: not only fluorenones **II** but also fluorenes **XXIV** and their alkylidene derivatives **XXVI** should be mentioned.
- Page 16, line 3: "... its ..." should be replaced by "... their ..."
- There should be a space between Scheme 15 caption and the following text.
- Scheme 22, compound **XLVII**: R is acyl (not alkyl).
- Scheme 22, compound **XLVIII**: The CH₃ substituent is missing in the position 3.
- Part 2.1.3. 1,2,3,4-Tetrasubstituted fluorenes: it should be added "... and fluorenones" (also fluorenones are covered).
- Scheme 27, compound **LXI**: -CH₂O₂Me should be -CO₂Me.

The part four of the Thesis ("Results and Discussion", 60 pp) represents the main body of the Thesis (along with the respective part six "Experimental Part"). The emphasis is given mostly on the development of synthetic methodologies for the preparation of a large collection of 1,2,3,4-tetrasubstituted fluorene derivatives and spirobifluorenes as well as di-/tetrasubstituted chimerical structures merging the spirobifluorene unit with 5,8-dihydroindeno[2,1-*c*]fluorene ("pentahelicene-like") or 7,10-dihydrobenzo[*c*]benzo[6,7]indeno[1,2-*g*]fluorene ("heptahelicene-like") scaffolds. All the target (di)spirobifluorene compounds were systematically characterised in particular by UV-Vis and fluorescence spectroscopy and also the respective quantum yields were determined. The conclusions drawn from experimental results are adequate and correct.

General comments:

- The synthesis of fluorene derivatives is based on Rh^I-catalysed [2+2+2] cycloisomerisation of diynols or triyndiols (comprising a tolane fragment with an internal triple bond susceptible to the nucleophilic attack). Thus, such systems might alternatively undergo 5-exo-dig addition of the hydroxy group across the activated triple bond. Did the author observe the formation of such side products (oxygen pentacycles)?
- The author uses systematically an incorrect term "isobestic point" instead of correct "isosbestic point" throughout the Thesis. However, the term "isosbestic point" is reserved for a situation when absorption at a certain wavelength in the UV-Vis spectrum does not change during a reaction. Here, the author just speaks about the same absorption at a specific wavelength in UV-Vis spectra in the case of different compounds.
- Scheme 45: It would be much better to specify substituents directly in the scheme.
- The author propose a certain degree of "planarisation" in 4-aryl substituted spirobifluorene derivatives in an excited state, e.g., at **11e** (Figure 9). However, the adjacent substituents will certainly prevent such a "planarisation" process. Are there any computational data available? In the cited example (ref. 48) there is no substituent in the position 3.
- Table 5-11: The captions should be better specified (and more informative).

- Page 65, paragraph 2, line 9: 1-iodopyrene should be 4-iodopyrene to correspond to the structure of **18d**.
- Numbering of compounds is too complex. The author mixes roman numerals (nowadays practically abandoned in the chemical literature), Arabic numerals, Arabic numerals combined with letters and specific codes (such as S1 or S2). Unification of a numbering system would be highly appreciated.
- Why the racemates of chimeric heptahelicene-like dispirobifluorenes **41a-c** were not resolved into enantiomers (for instance by chiral HPLC)? They should be configurationally stable and their chiroptical properties might be of a primary importance.
- The compound **23i**: Owing to a hindered atropisomerisation of the 1-naphthyl units attached, two diastereomers in this respect might exist. What's the barrier to atropisomerisation of 1-naphthyl units and which atropisomer prevails?

Evidently, the PhD Thesis by MSc. Reinhard Peter Kaiser presents a successful synthetic approach to the attractive non-planar aromatics that are promising fluorescent materials. It follows modern trends of contemporary science. Summing up, the submitted PhD Thesis meets the requirements for the PhD Thesis in organic chemistry and convincingly demonstrates both the ability of the author to conduct high-quality research in the respective area of science. Therefore, it provides clear evidence that the candidate is worthy of unconditional admission to the defence of his PhD Thesis.

Prague, 18 August 2018



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