

OPINION

by Dr. Plamen Angelov Angelov, Associate Professor at the Paisii Hilendarski University of Plovdiv
on a dissertation for the award of the educational and scientific degree 'doctor'
in the field of higher education 4. "Natural Sciences, Mathematics and Informatics" Professional field
4.2. "Chemical Sciences" Doctoral program "Analytical Chemistry"

Author: Dimitar Genchev Stoitsov

Topic: „NMR and vibrational spectra assignment for verification and elucidation of the structures of aromatic organic and metal-organic coordination compounds“

Scientific supervisors:

Prof. Dr. Plamen Nikolov Penchev – Paisii Hilendarski University of Plovdiv

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1. General presentation of the procedure and the doctoral student

By Order No. PD-22-1706 of 21.07.2025 of the Rector of the University of Paisii Hilendarski, I have been appointed as a member of the scientific jury in the procedure for the defense of a dissertation on the topic „NMR and vibrational spectra assignment for verification and elucidation of the structures of aromatic organic and metal-organic coordination compounds“ for the acquisition of the educational and scientific degree "doctor" in the field of higher education 4. Natural sciences, mathematics and informatics, professional field 4.2 Chemical sciences, doctoral program "Analytical Chemistry". The author of the dissertation is Dimitar Genchev Stoitsov - a full-time doctoral student at the Department of Analytical Chemistry and Computational Chemistry. The set of materials presented by Dimitar Genchev Stoitsov is in full compliance with the requirements of the Law on the State Administration of Scientific Research and Development of the Republic of Bulgaria and the regulations for its implementation, as well as with the regulations on the conditions and procedure for acquiring scientific degrees and for occupying academic positions at the Paisii Hilendarski University.

2. Relevance of the topic

The dissertation submitted for evaluation is in the field of structural organic analysis, mainly with application of nuclear magnetic resonance spectroscopy. Of lesser importance in the dissertation are the methods of vibrational (IR) spectroscopy. The topic is of permanent relevance, given the practically inexhaustible structural-analytical tasks posed by modern synthetic organic chemistry, as well as by the chemistry of natural compounds.

3. Knowledge of the problem

The author of the dissertation has shown a good knowledge of the issues in the chosen research area. Evidence of this is the literature review, which extends over 32 pages and includes 157 sources. The fundamental principles of NMR spectroscopy are examined, as well as the most important one-dimensional and 2D correlation methods. Brief information is also provided on the importance and application of the classes of organic compounds to which the substances analyzed by the author belong.

4. Characteristics and evaluation of the dissertation work and contributions

The dissertation work has a total volume of 144 pages. After a brief introduction and description of the goals and objectives, a concise and well-organized literature review is presented on the basic principles of NMR spectroscopy and the various NMR techniques. The literature review examines the classes of organic compounds to which the substances analyzed by the author belong, citing sources on methods for preparation, application and analytical problems. Information on some useful software products used in the confirmation and elucidation of organic structures is also included. The materials and methods used are presented as a separate second section. The results of the doctoral student's own research are well-organized and presented in the third section of the dissertation. A full reference of NMR spectral data for 23 organic compounds has been made, as well as a partial reference of vibrational data for these compounds. Errors in previously published and referenced NMR data for four of these compounds have been corrected. The studied compounds include fluorenylspirohydantoin, naphthopyranones, 2,4-dithiouracil and 2-thiouracil, metal complexes of Cu(II) and Au(III) with 2,4-dithiouracil, dispiroimidazolidine derivatives, anthranilamides and benzo[d]isoquinolinediones. As appendices, separate from the dissertation, images of all NMR spectra in PDF format are presented.

5. Assessment of the publications and personal contribution of the doctoral student

To date, the results obtained in the dissertation have been presented in four scientific publications. Three of them are indexed in the Web of Science and Scopus databases, and one – only in Scopus. Two of the publications are in journals with a quartile Q2 – Applied Sciences (IF = 2.5) and Crystals (IF = 2.4), and two others are in publications with a quartile Q4 – Molbank (IF = 0.4) and Bulgarian Chemical Communications (SJR Q4).

Some of the results in the dissertation are to be published at a later stage. In two of the articles published so far, Dimitar Stoitsov is the first author, and in the remaining two he is the second, which is a good indication of his personal contribution.

6. Abstract

The abstract fully corresponds to the dissertation, presenting the results and discussion of the dissertation work in a condensed form. The conclusions and generalizations made are in full agreement with the results described in the dissertation.

7. Critical notes, recommendations and questions

I recommend that the primary data from NMR measurements be shared in a publicly available data repository (e.g. Zenodo), since the applied spectral images are not suitable for careful analysis.

The literature review indicates the hybrid state of the C-atoms as a factor determining the chemical shift, but only the difference in the s-character of the hybrid orbitals is indicated as the reason, while the magnetic anisotropy has a significantly stronger influence here. In this context, it would be appropriate to indicate the relationship between the s-character of the hybrid orbital and the corresponding $^1J_{CH}$ constant.

In the section with own research, the origin of the analyzed molecules is not indicated. Only the author who performed the synthesis is indicated, without a synthetic scheme or citation to the original work.

In some places, the term chemical equivalence is incorrectly used instead of isochronicity (p. 83, p. 85).

The proposed in Fig. 18 (p. 96) tautomerism would affect more signals in the 1H and ^{13}C spectra of compound XIV, and not only the discussed signal assigned to position vi. This is probably an artifact of poor phase correction, and not a second adjacent HSQC correlation with the opposite sign. The ^{13}C and 2D correlation spectra of XIV given in the appendix do not seem to be aligned to an internal standard and the chaos in the slight deviations of the δ values has been carried over into the discussion on p. 97.

I have the following questions for the doctoral student:

1. When assigning the spectra of dispiroimidazolidine derivatives XI – XIV, signals with an atypically small shift were assigned to a vinyl-type CH group (position vi according to the adopted numbering): 2.40 – 2.72 ppm for 1H and 25.24 – 29.17 ppm for ^{13}C . Have other possibilities for the proposed structures been considered?
2. Do you exclude the possibility that the N and S atoms in the benzothiazepine ring of compounds XII and XIII are in swapped positions?

These critical remarks made do not spoil the overall good impression of the work.

CONCLUSION

The dissertation contains scientific and applied scientific results that represent an original contribution to science and meet all the requirements of the Act on the Development of the Academic Staff in the Republic of Bulgaria (ADSRB), the Regulations for the Implementation of the ADSRB and the relevant Regulations of the University of Plovdiv. The presented materials and results cover the specific requirements for acquiring the scientific and educational degree “doctor” in the field of analytical chemistry. The dissertation shows that the doctoral student Dimitar Genchev Stoitsov possesses in-depth theoretical knowledge and professional skills, demonstrating qualities and skills for independent

conduct of scientific research. Due to the above, I confidently give my positive assessment of the conducted research presented by the dissertation and propose to the esteemed scientific jury to award the educational and scientific degree “doctor” to Dimitar Genchev Stoitsov in the field of higher education: “Natural Sciences, Mathematics and Informatics”, professional field 4.2. “Chemical Sciences”, Scientific specialty “Analytical Chemistry”.

01.10.2025

Assoc. Prof. Dr. Plamen Angelov