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## REVIEW

of Doctoral Dissertation

authored by MSc Alejandro Iglesias Reguant

*entitled:*

*„Intermolecular Interactions Between Fluorophores Carrying  
BF/BF<sub>2</sub> Groups and Halogenated Fluorobenzenes”*



## General Remarks

The doctoral dissertation of MSc Alejandro Iglesias Reguant, entitled “*Intermolecular Interactions Between Fluorophores Carrying BF/BF<sub>2</sub> Groups and Halogenated Fluorobenzenes*” was prepared at the Faculty of Chemistry of Nicolaus Copernicus University in Toruń under the supervision of two advisors: Professor Borys Ośmiałowski, PhD, DSc (Chair of Organic Chemistry), and Dr. Joseph Maria Luis from the Institute of Organic Chemistry and Catalysis at the University of Girona. The dissertation was written in English in a traditional format, not as a commentary on a series of scientific papers; however, it is based on a series of three publications in which Alejandro Iglesias Reguant is the first author. These articles were published in high-ranking scientific journals: one paper in *J. Org. Chem.* and two papers in *Phys. Chem. Chem. Phys.* Additionally, the Doctoral Candidate is a co-author of next three publications, only one of which was published in a "predatory journal" - Molecular Diversity Preservation International (MDPI). I want to mention that statements from the co-authors about their roles in the papers are not included, though this information isn't required. However, upon comparing the content of the presented publications with this dissertation, it is, in my opinion, clear that the Author played a leading role in their development. Additionally, the fact that the Doctoral Candidate is listed as the first author in the presented publications indicates, in my view, that the material discussed in the publications is predominantly his intellectual contribution, thereby confirming compliance with the statutory requirement for the ability to conduct independent scientific research—a requirement for candidates seeking the doctoral degree. The language in which the dissertation is written is correct and clear, making it easy to read and follow the Author's line of reasoning without any difficulty. Despite careful scrutiny, I did not find any language issues or text composition errors.

The Author's results have been presented at scientific conferences, with some of these being oral presentations given by MSc Alejandro Iglesias Reguant, even though this fact is



not included in the documentation. As an attendee of one of such presentations, I can affirm that these presentations were of an exceptionally high standard. Therefore, I consider the Author's achievements to be substantial at this stage of his scientific career, placing him significantly above average.

The dissertation comprises only 110 pages, including the list of figures, tables, publications, bibliography, and supplementary materials, demonstrating that the Author values the importance of every word. However, it should be noted that within these 110 pages, the Author has managed to present an impressive volume of research findings. Following MSc Alejandro Iglesias Reguant as an example, I will also be succinct in my description of the substantive content.

Furthermore, it is essential to emphasize the accuracy, precision, and aesthetic quality of this work's composition; the document's preparation using TeX is a noteworthy aspect deserving of commendation. The figures are carefully crafted, highly readable and clearly convey their intended message. The tables are not overloaded with data, showcasing only the key aspects of the discussed spectroscopic/molecular details, which underscores the Author's considerable scientific maturity—there is no tendency to include every possible data point available.

### **Substantive scope of the dissertation**

The dissertation consists of six chapters, and its structure is typical for this type of work. After a three-page acknowledgments section—which is impressive and indicates that MSc Alejandro Iglesias Reguant has excellent qualifications for scientific work, as he has no trouble establishing collaborations and seeking academic assistance—there is an abstract, an introduction, methodology, objectives, and the presentation of results, which is divided into two chapters. Finally, the conclusions are presented.

Additionally, the Author included a list of acronyms for the terms used in the work in



the first part of the dissertation, and in the final section, there is a list of 169 bibliographic references, which are key scientific publications in the field under investigation.

In the brief summary of his work, MSc. Alejandro Iglesias Reguant clearly describes the aspect of chemistry his research focuses on, namely the use of computational chemistry/physics tools to investigate the impact of intermolecular interactions, specifically one selected interaction—halogen bonding—on the electronic and infrared spectra of organic dyes containing BF/BF<sub>2</sub> groups. A more detailed description can be found in Chapter Three, where the objectives of the work are outlined.

In the introduction, the Author provides a history of organic dyes, starting from ancient Egypt, moving through the Middle Ages, and finishing with the present day. He then goes on to discuss in detail a group of modern dyes based on BODPIY (4,4-difluoro-4-bora-3a,4a-diaza-s-indace), while also pointing out its drawbacks, such as low emission in the crystalline state. Since the doctoral research concerns the impact of halogen bonding, the Author does not omit a detailed description of this phenomenon.

The Author presents a comprehensive overview of the significance and progress in the understanding of halogen bonding (XB) as a type of non-covalent interaction, with particular emphasis on its important role in various scientific fields, such as biochemistry, crystal engineering, and photoresponsive materials. He highlights the characteristic features of halogen bonds, such as directionality, tunability, and hydrophobicity. In my opinion, this is a comprehensive description that includes citations of the most important works, such as those by Professor Peter Politzer and Professor Jane Murray. Finally, the Author discusses recent research revealing that halogen bonding influences the modulation of fluorescence in certain dyes in solution.

Now comes the description of the methodology. The description is brief but detailed. The doctoral candidate presents the computational techniques used and provides a detailed explanation of the method for determining interaction energies and their decomposition



schemes, without omitting the BSSE (CP) error. The Author concludes this section by describing the use of a static electric field (Finite Field - FF method). At this stage, we only know that the Author uses the SCS-MP2 method, so far software used is not specified.

At the beginning of the next chapter, which concerns the significant impact of halogen bonding on the spectroscopic properties of organic fluoroborates, we learn exactly what the Author was responsible for—performing all calculations and processing the results. The collaborators responsible for the synthesis and measurements are also listed. This information ensures that there is no doubt or ambiguity regarding the authorship. This is a great advantage, as many doctoral dissertations lack such information, even though it is crucial. We also learn that the Author will be using the DFT/TD-DFT method with the MN15 functional and the aug-cc-pVDZ-PP basis set. This is the only point where I am concerned that this was not mentioned earlier in the methodology section. The use of the dedicated MN15 functional and the large basis set clearly indicates the scientific maturity of the Author. We also learn that the doctoral candidate will use the Gaussian16 program, MOLPRO and a modified version of GAMESS. Such a wide range of techniques and programs used by the Author proves that Mr. Alejandro Iglesias Reguant knows exactly what He is doing and what He expects. More importantly, He knows that it is impossible to obtain very good results quickly and easily. I have no reservations about this part of the work - the Author discusses the obtained results very clearly, and when he finds a problem, he presents us with a method of solving it, and then solves this problem effectively. In the last paragraph of this chapter, the Author anticipated my question regarding the influence of effects related to dynamics on the studied spectra and the energy of interactions, stating that this is a future direction of research.

Now, the Doctoral Candidate moves on to Chapter Five, in which He presents the decomposition of changes in the IR spectrum induced by the influence of halogen bonding for the studied complexes. Here, we learn about the application of an innovative approach (Infrared Spectra Decomposition Analysis, IRS-DA), which addresses the issues of previous methods like EDA.



The Author is a co-author of this groundbreaking code. In here as in the preceding chapter, we are skillfully guides through the technical details and results obtained using this innovative approach to decompose the intensities of peaks in the IR spectrum. The only question that arose after reading this chapter, is how the Author obtained the half-widths of the peaks in the simulated infrared spectrum shown in Figure 5.1 (the figure caption does not mention the computational method either), as this is not directly mentioned?

## Summary and Conclusions

The doctoral dissertation presented for review is a highly valuable scientific work that has taken another step toward understanding the impact of halogen bonding on the electronic and infrared spectra of complex molecular systems, particularly the group of organic dyes studied by the Author. In conclusion, I am pleased to state that the doctoral dissertation I have reviewed is a complete work that clearly documents the high scientific competence of its Author in the broadly defined field of physical and theoretical chemistry. I have no doubt that the dissertation submitted for my evaluation fully meets the requirements set in the Act of 20<sup>th</sup> of July, 2018, on Higher Education and Science (as amended), and in the Regulation of the Minister of Science and Higher Education of 30<sup>th</sup> January, 2018, on the detailed procedure for conducting activities in doctoral, habilitation, and professorial proceedings (Journal of Laws of 2018 , item 261). Therefore, without hesitation, I propose to the High Council of the Discipline of Chemical Sciences at the Faculty of Chemistry, Nicolaus Copernicus University in Toruń, to admit MSc Alejandro Iglesias Reguant to the next stages of the doctoral procedure.

Furthermore, considering the high substantive level of the dissertation and its significant intellectual value, I propose to the High Council of the Discipline of Chemical Sciences at the Faculty of Chemistry, Nicolaus Copernicus University in Toruń, to award the doctoral



dissertation of MSc Alejandro Iglesias Reguant with distinction. In accordance with Resolution No. 94/2023 regarding the criteria for distinguishing doctoral dissertations at Nicolaus Copernicus University in Toruń, the Author of the dissertation meets all the conditions set by Article 1, item 5 of this document.

With best regards,  
Przemysław Dopieralski