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REVIEW OF THE CHAPTER "ORIGIN OF PUCKERING (BUCKLING) OF PLANAR HETEROCYCLES AND METHODS OF ITS SUPPRESSION" BY N.N. GORINCHOY AND I.B. BERSUKER

The chapter "Origin of Puckering (Buckling) of Planar Heterocycles and Methods of Its Suppression," authored by N.N. Gorinchoy and I.B. Bersuker, is a comprehensive and insightful contribution to the field of physical chemistry, with a strong emphasis on quantum calculations and computational chemistry. The two authors are well-known in the scientific community for their contributions to the understanding of the structure and reactivity of various classes of compounds, based on the consequences of the Jahn-Teller effect. Published as part of the monograph Heterocycles: Synthesis, Reactions and Applications by Nova Science Publishers, Inc. (2020), this chapter spans 60 pages and is structured into an Introduction, three main sections with eight subsections, Conclusions, and a list of 50 relevant references. The authors delve into the structural deviations of heterocyclic compounds, particularly focusing on the phenomenon of puckering or buckling, which significantly influences their properties. The chapter not only elucidates the mechanisms behind these distortions but also provides practical methods for their suppression and the restoration of planar configurations.

Introduction: Context and Significance

The chapter begins by highlighting the growing interest in two-dimensional (2D) and quasi-2D materials, such as graphene-like systems, for applications in electronics and materials science. Heterocyclic compounds, due to their unique structural and electronic properties, are of particular importance in this context. The authors emphasize that understanding the deviations from planarity in these systems-manifested as puckering or buckling-is crucial for tailoring their properties for specific applications in physics, chemistry, biology, and materials science. The chapter sets the stage by explaining how the instability of planar configurations in heterocycles is not merely a structural curiosity but a fundamental aspect that affects their reactivity, stability, and functionality.

Theoretical Framework: Pseudo Jahn-Teller Effect (PJTE)

The core of the chapter revolves around the Pseudo Jahn-Teller Effect (PJTE), which is identified as the primary cause of the instability of planar configurations in heterocyclic compounds. The authors provide a detailed explanation of how the PJTE induces out-of-plane distortions, emphasizing the relationship between the energy gap (Δ), the vibronic coupling constant (F), and the primary force constant (K_0). The instability condition, expressed as $\Delta < F^2/K_0$, serves as the foundation for understanding how external perturbations-such as ionization, excitation, redox processes, chemical substitutions, and coordination-can be used to manipulate the planarity of heterocyclic systems.

The authors demonstrate that, by calculating the electronic structure of these systems, identifying the PJTE-active excited states, and determining the relevant parameters, it becomes possible to suppress or enhance the distortions. This theoretical framework is not only elegant but also highly practical, as it provides a clear pathway for controlling the structural properties of heterocycles. The PJTE is presented as a unifying concept that explains a wide range of phenomena in heterocyclic chemistry, from the buckling of simple rings to the structural dynamics of complex polycyclic systems and extended 2D materials.

Section 1: Revealing the Excited States and PJTE Parameters

The first section focuses on the methodology for applying the PJTE theory to specific heterocyclic systems. Using the example of four hexa-heterocycles (1,4-$C_4N_2H_4X_2$, where X = H, F, Cl, Br), the authors illustrate how electronic structure calculations, including vibronic coupling, can reveal the key features responsible for out-of-plane distortions. These features include symmetrized atomic displacements, PJTE-active excited states, and energy gaps. The authors also show how the PJTE parameters can be estimated by fitting ab initio calculated energy profiles to the theoretical equations derived from the PJTE.

This section is particularly valuable for researchers in computational chemistry, as it provides a step-by-step guide to applying the PJTE theory to real-world systems. The authors emphasize the importance of accurate electronic structure calculations and the need to identify the specific excited states that contribute to the instability of planar configurations. By doing so, they provide a robust methodology that can be applied to a wide range of heterocyclic compounds.

Section 2: Methods of Suppression of PJTE-Induced Distortions

The second section is divided into three subsections, each exploring different methods for suppressing PJTE-induced distortions and restoring planar configurations in heterocyclic systems.

Suppression by Redox Influence and Excitation

The authors discuss how redox processes and electronic excitation can be used to suppress distortions. For instance, the planarization of thianthrene (a dibenzo-1,4-dithiin derivative) is achieved through oxidation, which reduces the vibronic coupling constant and stabilizes the planar configuration. Similarly, the introduction of nitrogen atoms into the thianthrene structure increases the energy gap between relevant molecular orbitals, thereby suppressing the PJTE and flattening the molecule. The redox influence is also analysed in tricyclic 1,2-dithiine systems, where reduction leads to significant structural changes, including the cleavage of S-S bonds and rotation of peripheral rings.

Suppression by Chemical Substitutions

Chemical substitutions are shown to be another effective method for controlling PJTE-induced distortions. For example, S-oxygenation of 1,4-dithiine derivatives can either suppress or enhance the PJTE, depending on the nature of the substitution. The authors also explore the effects of substitutions in heterosumanenes, where the replacement of carbon atoms with oxygen or sulphur atoms modulates the bowl-to-bowl inversion barrier and, consequently, the physical-chemical properties of these systems.

Suppression by Coordination

Coordination with external atoms or molecular groups is another powerful tool for suppressing distortions. The authors provide several examples, including the planarization of iron-porphyrin rings in haemoglobin upon oxygenation, the flattening of cyclohexasilane systems through the formation of dianions, and the suppression of PJTE in triple-decker sandwich structures by electron donation from molybdenum atoms. Additionally, the chapter discusses how aggregation and π-stacking interactions can weaken the PJTE in 1,4-dithiine systems, leading to planar configurations in the crystalline state.

Section 3: Applications to Extended 2D Systems

The final section extends the discussion to 2D materials, such as graphitic carbon nitride (g-C_3N_4), silicene, phosphorene, and germanene. The authors demonstrate how the PJTE can explain the buckling observed in these systems and suggest methods for restoring planarity. For example, the addition of Be^{2+} ions to g-C_3N_4 can suppress the PJTE and flatten the structure, while hydrogenation of germanene opens a large energy gap, enabling further chemical control.

The authors also discuss the case of 2D silicene, where intercalation with Li^+ ions suppresses the PJTE and results in a planar hexagonal structure similar to graphene. Similarly, the use of molecular dopants to influence the structural properties of phosphorene is analysed, highlighting the potential for targeted control of PJTE parameters. The chapter concludes with a discussion of germanene, where hydrogenation forms germanane, opening a large energy gap and providing a pathway for further chemical modifications.

Conclusion: Theoretical and Practical Implications

The chapter concludes by emphasizing the central role of the PJTE in understanding and controlling the structural properties of heterocyclic compounds and their 2D extensions. The authors highlight the practical applications of their theoretical framework, which enables the manipulation of planarity through targeted perturbations such as redox processes, chemical substitutions, and coordination. The reviewed examples span a wide range of systems, from simple heterocycles to complex polycyclic structures and extended 2D materials, showcasing the versatility of the PJTE approach.

The authors also stress the importance of integrating theoretical insights with experimental data, as this combination provides a more comprehensive understanding of the structural dynamics of heterocyclic systems. They suggest that future research should focus on exploring new methods for suppressing PJTE-induced distortions and applying these techniques to the design of novel materials with tailored properties.

Overall Assessment

This chapter is a remarkable synthesis of theoretical insight and practical application. The authors successfully bridge the gap between quantum chemical theory and experimental chemistry, providing a robust framework for understanding and controlling the structural properties of heterocyclic systems. The clarity of presentation, combined with the depth of analysis, makes this chapter an invaluable resource for researchers in organic synthesis, computational chemistry, and materials science. It is particularly relevant for those interested in designing novel heterocyclic compounds with tailored properties for advanced applications.

In summary, "Origin of Puckering (Buckling) of Planar Heterocycles and Methods of Its Suppression" is a significant contribution to the field, offering both fundamental insights and practical tools for the manipulation of heterocyclic systems. The chapter is highly recommended for researchers and graduate (PhD) students (seeking to deepen their understanding of the structural dynamics of heterocycles and their applications in modern science and technology.

The reviewers appreciate the authors for their thorough and insightful analysis, which is expected to have a lasting impact on the field of physic and heterocyclic chemistry. The chapter is a testament to the authors' expertise and their ability to present complex theoretical concepts in an accessible and practical manner.

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