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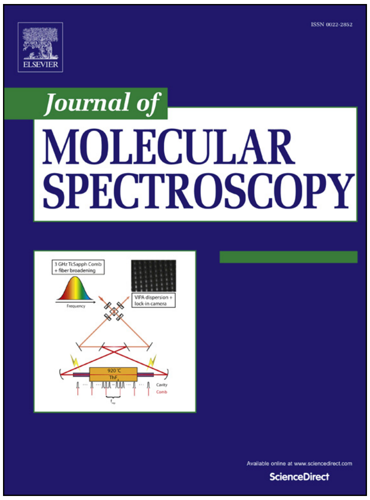

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Influence of the Position of the Methoxy Group on the Stabilities of the *Syn* and *Anti* Conformers of 4-, 5-, and 6-Methoxyindole.[☆]

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Abstract

Even though the two possible rotamers of methoxy-substituted indoles only differ in the orientation of a methoxy group, this slight geometry change can have a strong influence on the stabilities and further molecular properties of the conformers. In the present study, we evaluate the effect of the methyl group position on the presence of different conformers in molecular beam studies for the systems 4-, 5-, and 6-methoxyindole. By using rotationally resolved electronic Stark spectroscopy in combination with high level *ab initio* calculations the structures of the observable conformers have been assigned and reasons for the absence of the missing conformers discussed. Thereby, we could show that the relative ground state energies and isomerization barriers for both conformers strongly depend on the position of the methoxy group and are the main explanation for the absence of the *syn* conformers of 4-, and 5-methoxyindole.

Keywords:
Electronic spectroscopy, Structural analysis, *ab initio* calculations, Conformational preferences, Methoxyindoles

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1. Introduction

The basic concept that structure always precedes function has stimulated competing theories on molecular recognition like the older lock and key principle by Fischer,[1] the more recent concept of induced fit by Koshland,[2] and the conformational selection theory.[3] Today it seems confirmed that in many cases conformational selection is followed by conformational adjustment.[4] This means that allosteric binding at the receptor site of a protein induces a conformational change at another site. Thus, barriers to large amplitude motions have to be affected through the ligand molecule.

However, the term *structure* should include not only geometric effects on the interaction, but also electronic effects. Additionally, the magnitude and especially the direction of the permanent dipole moments in the electronic ground state strongly influence ligand-receptor interactions. In an intuitive picture the individual dipole moments of the polar groups in a molecule are summed vectorially, resulting in the overall dipole moment. However, Pratt and coworkers have shown that inductive effects may lead to breakdown of this rule.[5] Even for the electronic ground state theoretical predictions of electric dipole orientations can deviate considerably from the experimental one.[6],[7] Also electronic excitations have been shown to dramatically change molecular dipole moments, in some cases a complete reorientation was observed.[8]

For flexible molecules the dipole moment often depends on the specific conformation, stressing the influence of the conformational space. For methoxyindoles the problem of different rotamers in molecular beam experiments cannot be answered uniformly. In general, they can exist in two rotameric forms which are due to the two-fold internal rotation of the methoxy group about the CO bond. For 6-methoxyindole (6MOI) two electronic origins bands at 33 722 and 33 952 cm^{-1} were observed in resonant enhanced multiphoton ionization (REMPI) spectra.[9] Our group could show that the shorter wavelength band at 33 716.58 cm^{-1} belongs to the *anti* rotamer, the other band at 33 948.12 cm^{-1} to the *syn* rotamer.[10] However, the excitation spectrum of 5-methoxyindole (5MOI) shows just a single origin band which could be shown to be due to the *anti* conformer.[11],[12],[13] Also the laser induced fluorescence spectrum of 4-methoxyindole (4MOI) consists of a single origin band at 35 309 cm^{-1}.[12] Hence, the question arises why the number of observed conformers in molecular beam experiments depends on the position of the substituent.

Here, we will study the position-dependent stability of the *syn* and *anti* conformers of 4-, 5-, and 6-methoxyindole. The structures of all molecules are shown in Figure 1. Recently, the ground and excited state structures of 5MOI and 6MOI[13],[10] and the dipole moments of 5MOI[6] have been presented. In the current contribution, we will extend the investigation to 4MOI, present the dipole moments of 4MOI and 6MOI and compare the whole class of methoxyindoles.

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[☆] Dedicated to Walther Caminati

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