A Quantum Mechanical Approach to Electrochemical Behavior of Spirochromics

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ABSTRACT: Fully optimized semiempirical quantum-chemical calculations of photochromic spiropyrans are presented. The vertical ionization potentials are calculated and their variation with substitutions are correlated to experimental oxidation potentials. The effects of the substitutions are studied and the partial charges on indoline and pyran components generated by HOMO are found to be responsible for the variations. The deactivating groups on the indoline ring system and deactivating groups on the pyran system increase the ionization potential and, consecutively, the oxidation potential. © 1999 John Wiley & Sons, Inc. Int J Quant Chem 75: 111–117, 1999

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Introduction

Spiropyrans are compounds exhibiting photochromic properties and because of that they are widely used in various industrial applications such as photochromic glasses, nonlinear optics, and biological probes. Spirocompounds are very intensively studied either by chemical or electrochemical oxidation or reduction methods; especially, the nitro-substituted derivatives of these compounds are of interest since they are easily reducible species [1–3]. There have been various reports on the synthesis of the spiro compounds studied in this work [4–13] and, previously, we have also presented results on their characterization and cyclic voltammetric measurements [14]. Although there appeared many experimental studies on their synthesis, spectroscopic analysis, or applications due to the industrial importance of the spirochromic molecules, the number of theoretical studies in this area is very limited.

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