A model system with intramolecular hydrogen bonding: Effect of external electric field on the tautomeric conversion and electronic structures

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ABSTRACT

A new model tautomeric system with intramolecular hydrogen bonding is proposed. Geometry optimizations are performed at HF and MP2 levels and absorption spectra are simulated at TDDFT level. The MP2 level of theory was chosen for studying the effect of the external electric static field (EF) on the molecular electronic structure. The geometries of the tautomers as well as the transition states are fully optimized for each magnitude and for opposite directions of the applied EF. Upon variation of the electric field strength and polarity, it is possible to stabilize different tautomeric forms of the molecule. The dipole moment, HOMO–LUMO gap and the spatial distribution of the frontier orbitals are found to be sensitive to the EF strength and polarity and the different tautomeric structures are differently affected by the field. Elongation of the conjugated system providing a large number of possible tautomeric forms is also examined at HF level. Systems similar to the studied model system have potential use in the design of new molecular electronic devices.

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1. Introduction

The idea of using organic molecules as functional units in electronic devices has received great attention. The assumption of Aviram and Ratner [1] that a single organic molecule could perform as a molecular rectifier may be regarded as the beginning of molecular electronics. A wide variety of molecules have been suggested as molecular devices, such as molecular wires [2–4], molecular diodes [5,6], molecular storage devices [7,8], molecular switches [9–11] and molecular logic gates [12]. Among the various kinds of molecules that can act as molecular devices, conjugated organic molecules favor electron transport of charge carriers along the chain. Due to the delocalization of π-electrons along the chain backbone, particular electrical and optical properties (large non-linear optical responses) arise [13]. It is found that molecules having quinoid structure or molecules which acquire such a pattern after structural changes provoked by external factors like light, electrical field (EF) possess a high degree of electron delocalization, planarity and small energy gap [14]. These properties of such molecules can be used to design bridge units between donor–acceptor fragments of molecular wires. The presence or the rise of extended π-electronic conjugation of bridge units promote strong coupling between donor–acceptor fragments. Many theoretical studies are

devoted to the design of molecular devices by adopting first-principle studies of the effect of an applied external EF on their molecular properties such as electron transfer in conjugated molecular wires [15–19] and conformational dependencies [20,21], and they confirm that the above mentioned properties of bridge units favor a high conductivity in molecular wires.

Another concept for the achievement of the required molecular performance can be realized by tautomeric conversion via fast proton transfer reaction between keto and enol tautomeric forms, each of them with distinct molecular properties. An important feature in such a reaction mechanism is the coupling between the proton motion and the electron density redistribution known as Proton Coupled Electron Transfer (PCET) [22]. The application of EF in a specific direction may favor the proton transfer so as to obtain a tautomer with desired properties. Studies on tautomeric systems in EF are scarce [23–25].

In some cases the tautomeric forms are near in energy and the tautomerization barriers are low enough. Then the application of an external EF with an appropriate magnitude and direction could change the tautomeric equilibrium in the desired direction, that is, EF could be used as a tool to yield a tautomer with desired properties.

We propose a new model system with a possible keto-enol tautomerism. The structure consists of three different fragments – benzoxazolyl (**Bo**), hydroxypyridil (**Hp**) and indanedionyl (**Ind**) where **Hp** is regarded as a bridge (Fig. 1). The presence of different bridge units **Hp** (n = 1–3, Fig. 1) leads to a large number of possible

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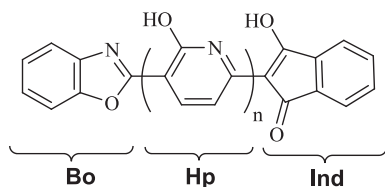 E-mail address: venelin@orgchm.bas.bg (V. Enchev).

Fig. 1. Structural formula of compounds **1** ($n = 1$), **2** ($n = 2$) and **3** ($n = 3$).

tautomeric forms as well as to a large number of possible tautomeric conversions between them. Detailed study of the EF effect on the electronic and geometric structure of compound **1** ($n = 1$, Fig. 1) is performed for understanding its molecular electrical properties.

2. Computational details

The geometries of the possible tautomers of 2-(5-(benzo[d]oxazol-2-yl)-6-hydroxypyridin-2-yl)-3-hydroxy-1H-inden-1-one (**1**) (Fig. 2) were located at HF and MP2 levels of theory with Pople's 6-31G(d,p) basis set using the quantum chemistry package, Firefly, version 7.1.H [26]. To investigate the chain length effect, 2-(5-(benzo[d]oxazol-2-yl)-2′,6-dihydroxy-2′,3′-dihydro-[2,3′-bipyridin]-6′(1′H)-ylidene)-1H-indene-1,3(2H)-dione (**2**) and 2-(5-(benzo[d]oxazol-2-yl)-2″,2″,6-trihydroxy-[2,3′:6′,3″-terpyridin]-6″(1″H)-ylidene)-1H-indene-1,3(2H)-dione (**3**) (see Fig. 1, $n = 2$, 3), were considered. Because of the size of the molecules, the calculations were performed at HF/6-31G(d,p) level. Li et al [27] have performed comprehensive tests at the HF level on the typical molecular wire, polyacetylene with a wide variety of basis sets, showing that HF/6-31G(d) is relatively "good", and can be used with sufficient accuracy and sustainable computing time.

Full geometry optimizations of the structures investigated were performed without symmetry constraints. The local minima and transition states were verified by establishing that the Hessians had zero and one negative eigenvalues, respectively. Starting from the transition state, the reaction path was generated as the steepest descent path in mass-scaled coordinates (intrinsic reaction coordinate, IRC) using the Gonzalez–Schlegel algorithm, employing
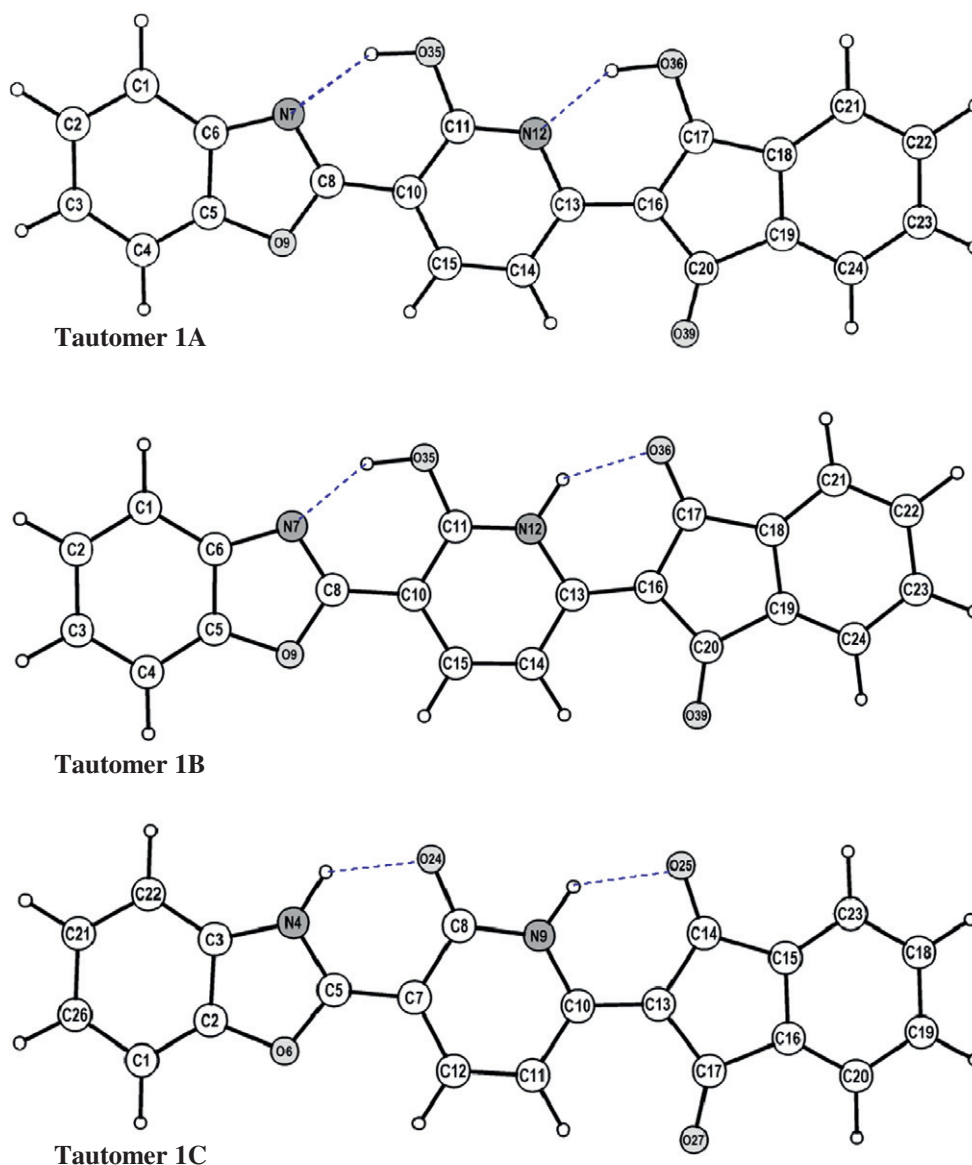

Fig. 2. MP2/6-31G(d,p) optimized structures of tautomers **1A–1C** with numbering of the atoms.