Organic Electronics 48 (2017) 154–164

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Theoretical study on the thermal *cis* - *Trans* isomerization of novel acylhydrazone photoswitches

Ting-Ting Yin, Zeng-Xia Zhao[*], Li-Ying Yu, Hong-Xing Zhang[**]

International Joint Research Laboratory of Nano-Micro Architecture Chemistry, Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, 130023 Changchun, China

A R T I C L E I N F O

Article history:
Received 21 April 2017
Received in revised form
15 May 2017
Accepted 31 May 2017
Available online 2 June 2017

Keywords:
DFT
Acylhydrazone
Substituent
Isomerization
Transition state

A B S T R A C T

Quantum chemical calculations of a potent class of photoswitches acylhydrazones have been carried out with the goal to describe their thermal *cis* → *trans* isomerization. The effects of substituents, in particular their number, position and nature of the substituents (electron donating/withdrawing groups (EDGs/EWGs)), on activation energies incorporating solvent effects have been systematically researched with the ultimate goal to illuminate the isomerization process. Our results show that most parameters are highly dependent on the substitution pattern on the crucial positions (R_1 and R_2 position) of the backbone fragment, which in turn has a significant impact on the absorption spectra, the energy levels of molecular orbitals, the transition properties for the *trans*/*cis* isomers, the half-lives $\tau_{1/2}$ and the rate constants for the thermal *cis* → *trans* isomerization of the compounds. In summary, both relative strength of the donor/accept groups and solvent polarity have significant impact on the electric properties. Finally, the nature of the transition state(s) and its dependence on substituents and the environment are discussed. An ingenious approach to the construction of reaction path was realized, and energy barriers were determined from two-dimensional potential energy surfaces of the ground states.

1. Introduction

Molecular photoswitches are ubiquitous in various fields ranging from the interface with biology and materials contexts [1–5], supramolecular and organic chemistry [6–8], photopharmacology and optochemical genetics [3,6,7] to materials science and data storage [6–9], all the way to the interface with physics [10–12]. In the past few decades, albeit it is clear to us that there exists several classes of these highly interesting functional molecules (azobenzenes, stilbenes, diarylethenes and spiropyrans, etc.) that have been heavily investigated and optimized, inherent limitations and distinct obstacles remain. Acylhydrazones as an innovative, yet under-exploited class of photochromic molecules based on the imine structural motif owns characteristic structural properties. As a result, the important and pervasive acylhydrazones have attracted much attention and were widely used in the past few decades from medicine, agriculture and chemistry as complexones [13], photo-thermochromic compounds and precursors for organic synthesis [14,15], to dynamic combinatorial chemistry [16] and covalent organic frameworks [17,18], etc. In many cases, properties and reaction ability of acylhydrazones are determined by their conformations and/or configurations. The existence of the carbonyl oxygen atoms and the imine nitrogen atoms in acylhydrazones encourages the formation of a chelate binding core. The facile synthesis, high stability enhanced stability toward hydrolysis in aqueous media and functional diversity of this azomethine group, which is characterized by the triatomic structure N—N=C, can be cited as reasons for their popularity.

The acylhydrazones functional group is perfectly suited to address the challenge as its *trans*/*cis* isomerization can be activated by both light and chemical inputs. This dual control over the rotary motion of a molecular system showcases the uniqueness of the acylhydrazone functional group. A quick survey of the structures of acylhydrazones (Fig. 1) reveal that configurational isomerism stemming from the intrinsic nature of the imine-like N=C double bond, altering the configuration and hence the steric and electronic relationship between the two parts on either side of the acylhydrazone center part (-N=C-) [19]. These structural motifs give acylhydrazone its chemical and physical properties, in addition to

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: zhaozx@jlu.edu.cn (Z.-X. Zhao), zhanghx@jlu.edu.cn (H.-X. Zhang).

http://dx.doi.org/10.1016/j.orgel.2017.05.053

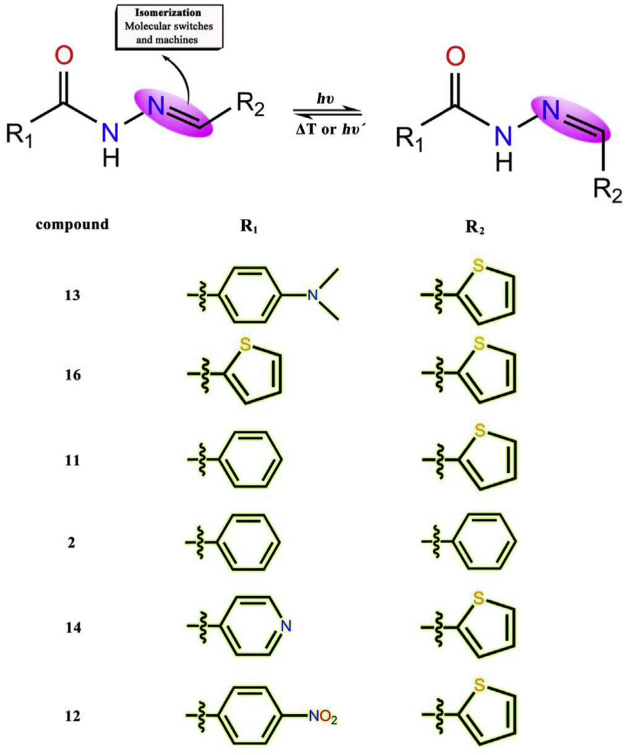

Fig. 1. Mechanism for *cis* → *trans* interconversion of acylhydrazone complexes investigated for structure-property relationship.

playing a vital part in determining the scope of applications it can be included in. Acylhydrazones produce an especial interesting scaffold, allowing more feasible photochemical isomerization than hydrazones [20] and acylhydrazone photoswitches have been testified invaluable in some intriguing applications [21]. Isomerization of acylhydrazones induces configurational change around the N=C double bond which similar to stilbene-, azobenzene-, and indigo derived photo-switches. Unlike azobenzenes [22,23], acylhydrazone photoswitches have lots of superior properties: (i) the geometry of both *trans*- and *cis*-acylhydrazone are tunable, which is a main advantage and provides a higher degree of control over their properties; (ii) acylhydrazones are more robust and resistant to oxidation; (iii) relative ease of synthesis from esters or acyl chlorides via their hydrazide precursors; (iv) importantly, their thermal stability can be controlled with no need to specifically stabilize the *cis*-isomers; (v) moreover, electron-donating and -withdrawing, heteroaromatic and large aromatic groups such functional groups could be introduced with no inhibiting the photochromic function, which opens the door to a good deal of applications to these photoswitches. However, acylhydrazones and their photoisomerization are far less researched, the systems reported in the literature thus far provide only scattered indications of photochromic properties of this class of compounds [24], including: Lehn [19,25,26] and Aprahamian's research [27–29]. Considerable synthetic efforts and complex structure-property relationship render the exploitation and development of this new photoswitches family difficult. Interestingly, in spite of a few reports have been investigated experimentally, however, concerning the thermal *cis* → *trans* isomerization there is not much known from the theoretical side. For a comprehensive review, we referred to the work of Hecht et al. [30], and relevant references are cited herein. They mostly designed and synthesized more than a dozen different photochromic molecules based on the imine structural motif acylhydrazones, bearing different substituents in all four crucial positions of the backbone fragment, exhibited some basic properties which they observed experimentally. But the data displayed here could not permit them to make comments on the property of the N=C isomerization (i.e., inversion vs. rotation). Inspired by the work of Hecht [30] and having this information in mind, we focused our attention on the elusive isomerization mechanism of acylhydrazones. We present herein a systematic study describing the effect of different substitutions on the overall performance of this new class of highly promising photoswitchable acylhydrazones (Fig. 1) by describing the effect of different substitution on the R_1 and R_2 positions, as well as assess the strong solvent impact on geometric and properties of acylhydrazones derivatives. The photochemical and photophysical properties of all compounds were investigated, together with the thermal stability of the *cis* forms using hybrid density functional theory (DFT). In particular, the vertical absorption spectra were computed using time-dependent DFT (TD-DFT) and thermal back-isomerization rates were predicted using Eyring transition-state theory, and last but not least, the preferred isomerization mechanism was investigated. This work may act as a systemic supplement that provides valuable insights for future experimental studies of searching highly promising photoswitches and guide the synthesis of new photoswitches with specific characteristics designed beforehand.

2. Computational details

2.1. Ground-state calculations

In this paper, we report quantum chemical calculations on acylhydrazone derivatives by conducting computational modeling of the *trans* and *cis* isomers of them. In order to further understand the effects of different substituents on the photophysical and photochemical properties of this class of complexes, six acylhydrazone derivatives were studied theoretically in this work. The donor strength is modified by substituting the R_1 and R_2 positions of such isomers with the groups depicted in Fig. 1. Among them is the parent acylhydrazone molecule **2**, starting from **2**, we focused on (i) change the nature of para-substituents on R_2 position (-phenyl or -2-thiophene); (ii) keep R_2 unchanged, we alter the nature of para-substituents on R_1 position (electron-donating groups or electron withdrawing groups). All calculations were performed using Gaussian 09 suite of programs [31]. All the stable structures and the transition states were fully optimized unrestrainedly by density-functional theory (DFT) [32,33] with the B3LYP [34] functional. More-over, all elements were assigned the 6-311++G(d,p) basis set based on the test of basis sets and computational costs consideration (Table S2). Solvent effect was simulated using the self-consistent reaction field (SCRF) method based on the polarizable continuum model (PCM) [39], with parameters taken from the acetonitrile (ACN). In order to assess the influence of solvent on the isomerization properties of the acylhydrazone complexes, solutions of **2**, **11**, **12**, **13**, **14** and **16** in solvents with varying polarities (gas phase, chloroform, THF, acetone, ethanol, acetonitrile, and water (increasing solvent polarity)) were prepared. Normal mode analysis of the transition structures delivered a single imaginary frequency, and the zero-point energy (ZPE) correction for each structure was obtained. Furthermore, the intrinsic reaction coordinate (IRC) theory was applied to identify the transition states connecting reactants and products. The natural bonding orbitals (NBO) analysis [40] was performed using NBO 3.1 program as implement in the Gaussian 09 package.

The kinetic parameters such as reaction rate constants of the thermal *cis* → *trans* isomerization at the temperature of 298.15 K (room temperature) were studied using conventional transition