

Solar energy storage in norbornadiene–quadricyclane system: electronic effects via ab initio computations

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Abstract

Electronic effects involved in the solar energy storage in norbornadiene (**1**)/quadricyclane (**2**) system, are investigated using ab initio methods at HF/6-31G* and DFT/6-31G* levels of theory. Substituents X, with various Hammett σ constants, are placed at the *para* carbon of a phenyl ring, attached to the C₂ of **1** and/or **2**. A Hammett ρ value of -0.81 is encountered; indicating that electron donating substituents ($-\text{NMe}_2$, $-\text{NH}_2$, $-\text{OMe}$, $-\text{OH}$ and $-\text{Me}$) induce storage of higher quantities of solar energy, than electron withdrawing groups ($-\text{NO}_2$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{CF}_3$ and $-\text{COOH}$).

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1. Introduction

Solar energy storage in norbornadiene (**1**)/quadricyclane (**2**) system, has attracted much attention, particularly as a mechanistic point of view [1–7]. Highly strained **2** has a potentially high energy, for containing a cyclobutane and two cyclopropane rings [8]. Conversion of **2** to **1** occurs through a radical-cation chain reaction route, initiated by chemical, electrochemical and photosensitized single-electron oxidations. The stored energy of **2** is released thermally [9]. The rearrangement of **1** to **2** occurs via the triplet state of **1** [9,10]. Low quantum yield (Φ) of this photo-conversion turns out to be the major drawback of this system [6,11]. Also, the **1/2** system has an inherent disadvantage of **1** not absorbing visible wave length of sunlight. Electron donating and/or electron withdrawing substituents, attached to the double bond of **1**, may provide a red shift of absorption, and increase the Φ value [12–14]. The water soluble carbamoyl and carboxyl derivatives of **1** and **2** are also used to absorb light of wavelengths longer than 300 nm [15]. Besides the usage of chromophores, using sensitizers is another method

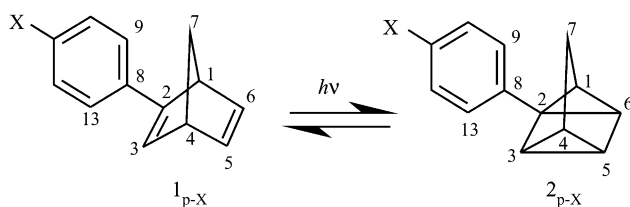
for solving the problem of not absorbing the visible light. Iridium complex is proposed as the sensitizer for $\pi-\pi^*$ excitation [4]. Density functional calculations with the hybrid B3LYP functional have been used to study the ground state of **1** bound to the photo-sensitizer [Cu(8-oxoquinolino)] [16]. Ab initio is used to study energetic of **1** and **2** conversions [17–19]. Up to date, no systematic ab initio calculations of donor-acceptor effects on **1/2** system are reported. In this work, electronic effects on the solar energy storage of substituted norbornadiene (**1_{p-X}**)/substituted quadricyclane (**2_{p-X}**) are reported using HF and B3LYP methods, for X = $-\text{NO}_2$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{CF}_3$, $-\text{COOH}$, $-\text{NMe}_2$, $-\text{NH}_2$, $-\text{OMe}$, $-\text{OH}$, $-\text{Me}$ (Scheme 1).

2. Computational methods

A quest for higher storage of the solar energy is carried out, for substituted norbornadienes (**1_{p-X}**) and quadricyclanes (**2_{p-X}**) system, via ab initio (Scheme 1). Geometry optimizations are performed by HF and B3LYP [20,21] methods using 6-31G* basis set of the GAUSSIAN 98 system of programs [22]. The HF/6-31G* optimized geometrical outputs are used as inputs for the B3LYB/6-31G* calculations. This is for obtaining more accurate values of

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Scheme 1. The solar energy storage system of substituted norbornadiene (1_{p-X})/substituted quadricyclane (2_{p-X}); where $X = -NO_2, -F, -Cl, -Br, -CF_3, -COOH, -NMe_2, -NH_2, -OMe, -OH$ and $-Me$.

activation electronic energies (ΔE), enthalpies (ΔH) and Gibbs free energies (ΔG). In order to find energy minima, keyword 'FOPT' is used. This keyword requests that a geometry optimization be performed. The geometry will be adjusted until a stationary point on the potential surface is found. Here, the Berny algorithm is employed for all minimizations, using redundant internal coordinates [23]. For minimum state structures, only real frequency values are accepted. The calculations exhibit systematic errors and thus benefit from scaling. Thermodynamic functions obtained through frequency calculations, are multiplied by the scaling factor of 0.89 suggested by Hehre et al. [24] for HF/6-31G*; and by 0.99 scaling factor of Rauhut and Pulay [25] for B3LYP/6-31G*. This is to account for the difference between the harmonic vibrational calculations and the anharmonic oscillations of the actual bonds. Nevertheless, scaling factors fitted to the observed (anharmonic) frequencies will deviate from unity even for exact calculations [26]. Here, a set of molecules containing similar motifs are treated together, where they benefit from similar scalings. The Hammett σ_{para} substituent constants are employed in order to figure out the Hammett ρ value for the conversion of 1_{p-X} to 2_{p-X} [27].

3. Results and discussion

The objective of this study is to determine the electronic effects, on the solar energy storage in norbornadiene (1)–quadricyclane (2) system, using ab initio methods at HF/6-31G* and DFT/6-31G* levels of theory. Taking into consideration the size of molecules probed, and the consistency of the results obtained, these ab initio calculation levels seem to be suffice. The extend of the solar energy stored in this system is measured simply by calculating the energy difference between the ground states of 1 and 2, without having any need to consider the excited states and/or the type of the mechanism involved. Both electron withdrawing and electron donating substituents are investigated. These substituents (X) are situated only at *para* carbons of phenyl rings, that are in turn attached to the C_2 of 1_{p-X} and/or 2_{p-X} (Scheme 1). Substituents attached at the *ortho* and/or *meta* positions are excluded because of showing the concurrent involvement of both steric and electronic effects. The C_2 position is reported in this

manuscript, since C_2 proved to be more sensitive to the substituent effects than carbons C_1 and/or C_7 . Nevertheless, an account of substituent effects at C_1 and C_7 as well as substitution at the *meta* positions will be presented in the near future. The thermal and electronic energies (E), enthalpies (H) and Gibbs free energies (G) for optimized structures of 1_{p-X} and 2_{p-X} are presented at HF/6-31G* and B3LYP/6-31G* levels of theory, where thermodynamic functions obtained through frequency calculations, are multiplied by the scaling factor of 0.89 suggested by Hehre et al. [24] for HF/6-31G*; and by 0.99 scaling factor of Rauhut and Pulay [25] for B3LYP/6-31G* (Table 1). The calculated harmonic force constants and frequencies are usually higher than the corresponding experimental quantities, at the ab initio SCF level, due to a combination of electron correlation effects and basis set deficiencies. The overestimation of the frequencies becomes more severe if the calculated harmonic frequencies are compared with the observed fundamentals, as anharmonicity usually lowers the frequencies [26,28]. Here, a set of molecules containing similar motifs are treated together, where they benefit from similar scalings.

Both electron withdrawing groups ($X = -NO_2, -F, -Cl, -Br, -CF_3$ and $-COOH$) and electron donating substituents ($X = -NMe_2, -NH_2, -OMe, -OH$ and $-Me$) appear to stabilize both 1_{p-X} and 2_{p-X} . Stabilization of 1_{p-X} may be attributed to the possibility of extension of conjugation through conglomeration of *p-X*-phenyl with the $C=C$ of norbornadiene. The stabilization of 2_{p-X} may be explained using the Walsh orbital model, where the cyclopropyl ring may act both as a good π donor and a good π acceptor [29].

Energy gaps between 1_{p-X} and 2_{p-X} , which are measures of solar energy storages in the system, are calculated (Table 2). Solar energy storage increases the most by electron donating substituents attached at phenyl- C_2 of 1_{p-X} and 2_{p-X} . A linear free energy relationship is observed upon plotting the energy gaps between 1_{p-X} and 2_{p-X} ($\Delta E_{1p-X-2p-X}$) vs. the Hammett σ_{para} substituent (X) constants [27]; showing a Hammett ρ value of -0.81 with a correlation factor $R^2 = 0.97$ (Chart 1). In other words, The Hammett ρ value is obtained through plotting $\sigma_{para}/\Delta E_{(1p-X)-(2p-X)}$ for: $-NO_2$ (0.78/22.065), $-CF_3$ (0.54/22.303), $-COOH$ (0.45/22.231), $-F$ (0.06/22.667), $-Cl$ (0.23/22.515), $-Br$ (0.23/22.496), $-H$ (0.00/22.598), $-Me$ ($-0.17/22.760$), $-OH$ ($-0.37/22.800$) and $-NMe_2$ ($-1.23/23.814$) (Chart 1).

The Mulliken charges on carbon atoms of 1_{p-X} and 2_{p-X} are presented (Table 3). The increasing trend of charge on C_3 in 1_{p-X} , as a function of *p-X* is: $1_{p-N(CH_3)_2} < 1_{p-OCH_3} < 1_{p-OH} < 1_{p-CH_3} < 1_{p-Br} < 1_{p-Cl} < 1_{p-F} < 1_{p-H} < 1_{p-COOH} < 1_{p-CF_3} < 1_{p-NO_2}$ (Table 3). This trend more or less follows the order of Hammett σ_{para} substituent constants [27]. The lowest charge on C_3 is observed for $X = p-N(CH_3)_2$, while the highest charge is encountered for $X = p-NO_2$. Apparently, direct resonance of *p-N(CH_3)_2* with $C_2=C_3$ places an electron density on C_3 , while *p-NO_2* depletes electron density from the same carbon, through a similar electron

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