

SHORT COMMUNICATION

STERIC EFFECT STUDIES ON SOLAR ENERGY STORAGE OF NORBORNADIENE- QUADRICYCLANE SYSTEM: DFT CALCULATIONS

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ABSTRACT. The aim of this research is to determine the possible solar energy storage in the norbornadiene (**1**) / quadricyclane (**2**) system, through involving steric effects on various position of carbon C₁, C₂ or C₇ for **1** and **2**; calculating the corresponding energies at B3LYP/6-311G** level of theory. The extent of the solar energy storage is the least for **1**_{1-i-Pr} (-21.018), **1**_{2-i-Bu} (-22.525) and **1**_{7-i-Pr} (-17.753) when the bulk substituents (X) were occurred at C₁, C₂ and C₇, respectively.

KEY WORDS: Solar energy, Energy storage, Norbornadiene, Quadricyclane, Steric effect, DFT calculation

INTRODUCTION

Solving today's energy problems through the employment of the environmentally safe "solar energy" has received much attention [1]. Intramolecular photochemical [2 π -2 π]-cycloaddition of norbornadiene, **1**, to quadricyclane, **2**, has been studied as a mechanistic point of view [2-4]. The conversion of quadricyclane, **2**, to norbornadiene, **1**, leads to generate heat energy. The **1/2** system is used for solar energy storage [5-7], in molecular switching [8-10], in optoelectronic devices [11-14], as a data storage compound [15, 16], as photodynamic chemosensor for metal cations [17, 18], as a potential photoresponsive organic magnet [19-21] and as an energetic binder for solid rocket propellants [22]. Use of sensitizers and chromophores on **1/2** system are two developments to maximize the solar energy storage [23]. Iridium complex is proposed as the sensitizer for π - π^* excitation [4]. The donor-acceptor chromophores are placed at the double bond of the norbornadiene molecule. *Ab initio* is used to study energetic of **1** and **2** conversions [4, 24, 25]. DFT calculations have been used to study the ground state of **1** bound to the photosensitizer [Cu(8-oxoquinolino)] [26].

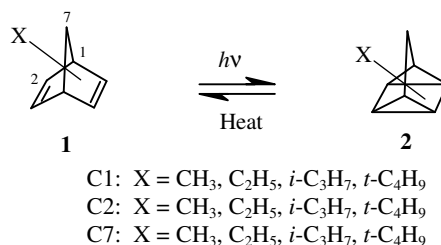
As a continuation of our investigation [27, 28], we report the photochemical energy storage in the ground states of **1/2** system through involving steric effects at various positions of **1** and **2** in this communication.

COMPUTATIONAL METHODS

The molecular structures of n-substituted norbornadienes (**1**_{n-x}) and n-substituted quadricyclanes (**2**_{n-x}), shown in Scheme 1, are studied using *ab initio* methods. Geometry optimizations are carried out by B3LYP [29, 30] method using 6-31G* basis set of the *Gaussian* 98 system of programs [31]. The B3LYP/6-31G* optimized geometrical outputs were used as inputs for the B3LYP/6-311G** calculations were carried out due to obtain more accurate energies. This is for obtaining more accurate values of activation electronic energies (E), enthalpies (H) and Gibbs free energies (G). The Bery algorithm was employed for all minimizations using redundant internal coordinates [32]. For minimum state structures, only real frequency values were accepted. All calculations were carried out for gas phase at 298 K temperature and 1 atm

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pressure. The calculations exhibit systematic errors and thus benefit from scaling. Thermodynamic functions obtained through frequency calculations, were multiplied by Hehre *et al.* [33] scaling factor of 0.89 for HF; and by 0.99 scaling factor of Rauhut and Pulay [34] for B3LYP. 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 observe (anharmonic) frequencies will deviate from unity even for exact calculations. Here, a set of molecules containing similar motifs was treated together, where they benefit from similar scalings.



Scheme 1. Storage of solar energy in X-norbornadiene ($\mathbf{1}_{n-X}$) / X-quadracyclane ($\mathbf{2}_{n-X}$) system; where X = -H, -Me, -Et, -*i*-Pr and -*t*-Bu.

RESULTS AND DISCUSSION

Recently we have reported theoretical investigations on the electronic effects involved in the solar energy storage, for substituents “indirectly” attached to the C₂ of $\mathbf{1}$ and/or $\mathbf{2}$, and “directly” attachment of the substituents at C₁, C₂ or C₇ atoms of $\mathbf{1}$ and $\mathbf{2}$ [27, 28]. However, the steric effects of various alkyl groups at different position of $\mathbf{1}$ and $\mathbf{2}$, which appear of “practical interest” to those whose primary goal is to replace the fossil fuel and/or the nuclear energy with the most economical and very available solar energy, have not been investigated. In this paper we studied the photochemical energy storage in the ground states of $\mathbf{1}_{n-X}$ / $\mathbf{2}_{n-X}$ system (X attached at carbons C₁, C₂ or C₇; n = 1, 2 or 7, respectively) with substituting of various bulk groups at different position of $\mathbf{1}_{n-X}$ and $\mathbf{2}_{n-X}$.

The thermal and electronic energies (E), enthalpies (H) and Gibbs free energies (G) for optimized structures of $\mathbf{1}_{n-X}$ and $\mathbf{2}_{n-X}$ (X = -H, -Me, -Et, -*i*-Pr and -*t*-Bu; X is a bulky substituents at carbons C₁, C₂ or C₇; n = 1, 2 or 7, respectively) was calculated at B3LYP/6-31G* and B3LYP/6-311G** levels of theory. Considering the size of molecules probed, and the consistency of the results obtained, these *ab initio* levels proved to be appropriate. For the sake of brevity, only the data acquired through the highest level of theory B3LYP/6-311G** was reported (Table 1).

B3LYP/6-311G** calculations indicated that the stability of all norbornadienes, $\mathbf{1}_{n-X}$, seem to be more than their corresponding quadracyclanes, $\mathbf{2}_{n-X}$.

The absolute stability of $\mathbf{1}_{n-X}$ as well as $\mathbf{2}_{n-X}$, are the most when substituents (X) were occurred at C₂ carbon (n = 2), and the least when the substituents (X) were occurred at C₇ carbon atom (n = 7) (Table 1). The stability changes for $\mathbf{1}_{n-X}$ as well as $\mathbf{2}_{n-X}$ are in the order: C₂ > C₁ > C₇.

The higher stability at C₂ of $\mathbf{1}_{n-X}$ is mainly attributed to the possibility of extension of hyperconjugation of C=C by the attached alkyl substituents. The stabilization of $\mathbf{2}_{n-X}$ by alkyl substituents (X) at cyclopropyl rings are mostly explained by the Walsh orbital model, where cyclopropyl rings may act both as good π donors and good π acceptors [27, 35].

Table 1. The B3LYP/6-311G** thermal and electronic energies (E), enthalpies (H), and Gibbs free energies (G), in kcalmol⁻¹, for optimized X-norbornadienes (**1_{n-X}**) and X-quadracyclanes (**2_{n-X}**); where X = -H, -Me, -Et, -i-Pr and -t-Bu.

n-X (n = 1, 2, 7)	1_{n-X}		
	E	H	G
1-H	-170233.037	-170232.445	-170253.747
1-Me	-194875.870	-194875.277	-194898.638
1-Et	-219514.575	-219513.982	-219539.430
1-i-Pr	-244153.902	-244153.310	-244180.561
1-t-Bu	-268793.473	-268792.881	-268821.670
2-H	-170233.037	-170232.445	-170253.747
2-Me	-194877.742	-194877.150	-194900.785
2-Et	-219516.624	-219516.032	-219541.859
2-i-Pr	-244156.771	-244156.179	-244183.849
2-t-Bu	-268796.714	-268796.121	-268825.252
7-H	-170233.037	-170232.445	-170253.747
7-Me	-194873.882	-194873.290	-194896.598
7-Et	-219509.241	-219508.648	-219533.952
7-i-Pr	-244148.909	-244148.316	-244175.578
7-t-Bu	-268788.728	-268788.135	-268817.016
n-X (n = 1, 2, 7)	2_{n-X}		
	E	H	G
1-H	-170210.782	-170210.189	-170231.175
1-Me	-194853.660	-194853.068	-194876.165
1-Et	-219492.777	-219492.185	-219517.503
1-i-Pr	-244132.947	-244132.354	-244159.543
1-t-Bu	-268771.123	-268770.530	-268799.335
2-H	-170210.782	-170210.189	-170231.175
2-Me	-194854.702	-194854.109	-194877.322
2-Et	-219494.015	-219493.423	-219518.836
2-i-Pr	-244134.069	-244133.476	-244160.790
2-t-Bu	-268774.393	-268773.800	-268802.726
7-H	-170210.782	-170210.189	-170231.175
7-Me	-194851.902	-194851.309	-194874.370
7-Et	-219489.491	-219488.899	-219514.053
7-i-Pr	-244131.102	-244130.509	-244157.825
7-t-Bu	-268769.767	-268769.175	-268797.886

Extent of the solar energy stored in this system is measured simply by calculating the energy gaps between the ground states of **1_{n-X}** and **2_{n-X}**. Evidently, there was no practical need to consider the excited states and/or the type(s) of the mechanism involved. Thermal energy gaps, $\Delta E_{(1n-X)-(2n-X)}$, enthalpy gaps, $\Delta H_{(1n-X)-(2n-X)}$ and free energy gaps, $\Delta G_{(1n-X)-(2n-X)}$, in kcalmol⁻¹, between X-norbornadienes (**1_{n-X}**), and their corresponding X-quadracyclanes (**2_{n-X}**) are calculated (Table 2).

Free energy gaps between **1_{n-X}** and **2_{n-X}**, $\Delta G_{(1n-X)-(2n-X)}$, is the least for **1_{1-i-Pr}**, **1_{2-t-Bu}** and **1_{7-i-Pr}** when the substituents (X) were occurred at C₂, C₂ and C₂, respectively (Table 2). Calculated free energy gaps between **1_{n-X}** and **2_{n-X}**, $\Delta G_{(1n-X)-(2n-X)}$, indicate extent of solar energy storage in X-norbornadienes (**1_{n-X}**)/X-quadracyclanes (**2_{n-X}**) system. Therefore, extent of solar energy storage is the least for **1_{1-i-Pr}** (-21.018), **1_{2-t-Bu}** (-22.525) and **1_{7-i-Pr}** (-17.753) (in kcal/mol) when the substituents (X) were occurred at C₂, C₂ and C₂, respectively (Table 2). The solar energy storage changes for compounds **1_{1-X}** are in the order: -H (-22.572) > -Me (-22.472) > -t-Bu (-22.335) >

-Et (-21.927) > -*i*-Pr (-21.018). Also, the solar energy storage changes for compounds $\mathbf{1}_{2-X}$ as well as $\mathbf{1}_{7-X}$ is in the order: -Me (-23.462) > -*i*-Pr (-23.060) > -Et (-23.023) > -H (-22.572) > -*t*-Bu (-22.525); and -H (-22.572) > -Me (-22.229) > -Et (-19.899) > -*t*-Bu (-19.130) > -*i*-Pr (-17.753), respectively.

Table 2. The B3LYP/6-311G** calculated thermal energy gaps, $\Delta E_{(1nX) - (2nX)}$, enthalpy gaps, $\Delta H_{(1nX) - (2nX)}$ and free energy gaps, $\Delta G_{(1nX) - (2nX)}$, in kcalmol⁻¹, between X-norbornadienes ($\mathbf{1}_{n-X}$) and X-quadracyclanes ($\mathbf{2}_{n-X}$); where X = -H, -Me, -Et, -*i*-Pr and -*t*-Bu.

n-X (n = 1, 2, 7)	$\mathbf{1}_{n-X}$		
	ΔE	ΔH	ΔG
1-H	-22.256	-22.256	-22.572
1-Me	-22.210	-22.210	-22.472
1-Et	-21.798	-21.798	-21.927
1- <i>i</i> -Pr	-20.956	-20.956	-21.018
1- <i>t</i> -Bu	-22.350	-22.350	-22.335
2-H	-22.256	-22.256	-22.572
2-Me	-23.041	-23.041	-23.462
2-Et	-22.609	-22.609	-23.023
2- <i>i</i> -Pr	-22.703	-22.703	-23.060
2- <i>t</i> -Bu	-22.321	-22.321	-22.525
7-H	-22.256	-22.256	-22.572
7-Me	-21.981	-21.981	-22.229
7-Et	-19.750	-19.749	-19.899
7- <i>i</i> -Pr	-17.807	-17.807	-17.753
7- <i>t</i> -Bu	-18.961	-18.960	-19.130

The changes of free energy gaps, $\Delta G_{(1nX) - (2nX)}$, between $\mathbf{1}_{n-X}$ and $\mathbf{2}_{n-X}$, could be related to stability and/or instability of each $\mathbf{1}_{n-X}$ and/or $\mathbf{2}_{n-X}$. However, one could not conveniently compare the absolute energies for compounds with different molecular formula. The stability and/or instability each of $\mathbf{1}_{n-X}$ and/or $\mathbf{2}_{n-X}$ may be described through comparing of their corresponding relative energies (Table 1).

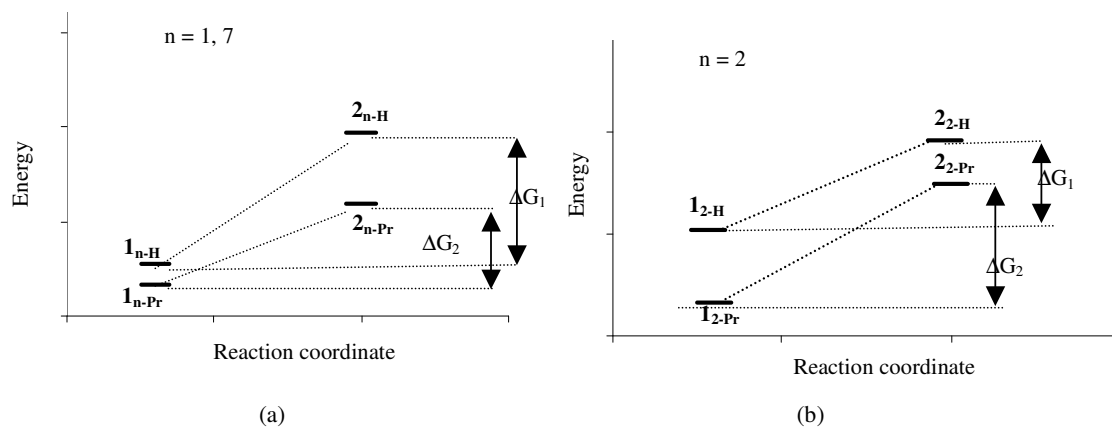


Figure 1. Reaction coordinate diagram for X-norbornadienes ($\mathbf{1}_{n-X}$) and X-quadracyclanes ($\mathbf{2}_{n-X}$).

Comparing of relative energies, one could conclude that the least $\Delta G_{(1n-x)-(2n-x)}$ energy is attributed to higher stability of 2_{n-x} respect to 1_{n-x} when bulk substituents (X) are occurred at C₁ and C₇ carbon atom (n = 1 and 7) (Figure 1a). In contrast, the high $\Delta G_{(1n-x)-(2n-x)}$ energy is attributed to higher stability of 1_{2-x} (except for 1_{2-t-Bu}) respect to 2_{2-x} when bulk substituents (X) are occurred at C₂ (n = 2) (Figure 1b).

Finally, it could be conclude that highest solar energy storage is in 1_{2-Me} and the least solar energy storage in 1_{7-i-Pr} .

CONCLUSIONS

The thermal energy gaps, $\Delta E_{(1n-x)-(2n-x)}$, enthalpy gaps, $\Delta H_{(1n-x)-(2n-x)}$ and free energy gaps, $\Delta G_{(1n-x)-(2n-x)}$, in kcalmol⁻¹, between X-norbornadienes (1_{n-x}), and their corresponding X-quadracyclanes (2_{n-x}) are presented using B3LYP/6-311G** level of theory. Free energy gaps between 1_{n-x} and 2_{n-x} , $\Delta G_{(1n-x)-(2n-x)}$, is the least for 1_{1-i-Pr} , 1_{2-t-Bu} and 1_{7-i-Pr} when the substituents (X) were occurred at C₁, C₂ and C₇, respectively.

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