NOTE

UV-Visible Absorption Study of Four-Substituted Norbornadiene-Quadricyclane System Through DFT Calculations

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UV-visible absorption studies of norbornadiene (**1_x**)/quadricyclane (**2_x**) system were carried out by density functional theory (DFT), method using 6-311++G** basis set of the GAUSSIAN 98 program. The DFT calculations indicate that the solar absorption bands of norbornadiene were shifted to the visible spectrum region through the electron withdrawing substituents more than through electron donating substituents.

Key Words: UV-visible absorption, Norbornadiene, Quadricyclane, Electron donating, Electron withdrawing.

Photoisomerization of norbornadiene (**1**) to quadricyclane (**2**) has been considered as an effective way to store solar energy¹⁻³. In this reaction, the energy stored in one mole of **2** is about 89 kJ due to its highly-strained structure. The stored energy can be released through the inverse reactions. Compound **2** could be considered as a potential high-energy density liquid fuel for the replacement of current fossil fuels. In continuation of our reports³⁻⁶, in this work UV-visible absorption study of four-substituted norbornadiene-quadricyclane system was carried out through DFT calculations.

Full geometry optimizations of norbornadiene (**1_x**)/quadricyclane (**2_x**) system were carried out by density functional theory (DFT), method using 6-311++G** basis set of the GAUSSIAN 98 program⁷⁻⁹ (**Scheme-I**). To find a global minimum on a specific surface, all possible conformations of the given species were examined through scanning the specific dihedral angles at B3LYP/6-311++G** level. All calculations were carried out for gas phase at 298 K and 1 atm.

In this work, we studied the photochemical energy storage of **1_x/2_x** (X = -NH₂, -OH, -CO₂H, -CONH₂ and CN) system with pull-pull, push-push and pull-push substituents (**Scheme-I**). We found that the carbon atoms, C₂, C₃, C₅ and C₆ were more sensitive to substituent effect than C₁, C₄ and/or C₇^{3,4}. Thus, we selected the carbon atoms C₂, C₃, C₅ and C₆ to investigation of UV-visible absorption. The thermal energy gaps, $\Delta E_{(1x)-(2x)}$, enthalpy gaps, $\Delta H_{(1x)-(2x)}$ and free energy gaps, $\Delta G_{(1x)-(2x)}$, in kcal mol⁻¹, between norbornadienes (**1_x**) and their

Scheme-I: Norbornadiene (**1_x**) and quadricyclane (**2_x**) where X = -CO₂H, -CONH₂, -CN, -NO₂, -OH and -NH₂

corresponding quadricyclanes (**2_x**) have been presented^{3,4}. DFT calculations indicated that the Gibbs free energy gaps between **1_x** and **2_x**, $\Delta G_{(1x)-(2x)}$, was the least when two electron withdrawing substituents and electron donating substituents (pull-push) were attached at both carbon atoms of the double bond C₂=C₃ and C₅=C₆, respectively. The $\Delta G_{(1x)-(2x)}$, was the most when four electron donating substituents (push-push) were attached at the double bond C₂=C₃ and C₅=C₆. However, the $\Delta G_{(1x)-(2x)}$, was increased when the electron withdrawing substituents (pull-pull) were attached at two sides of the double bonds C₂=C₃ and C₅=C₆.

The excited states of **1_x** could be related to their corresponding the UV-visible absorption (Table-1). Despite the importance of achieving the maximum stored solar energy by a chromophore or substituent, the absorption wavelength region was also important which was suitable when was shifted to the visible region. Therefore, the effects of both electron

TABLE-1
B3LYP/6-311++G** CALCULATED SOLAR ENERGY ABSORPTION FREQUENCY (cm⁻¹) AND THEIR INTENSITY (IN PARENTHESIS) FOR OPTIMIZED X-NORBORNADIENES (**1_x**); WHERE X = -NO₂, -CN, -CONH₂, -NH₂ AND -OH

(Compound)	Wavelength (intensity)					
1_{NO2}	303.89 (0.003)	304.64 (0.000)	317.05 (0.019)	317.06 (0.000)	343.55 (0.003)	349.65 (0.000)
1_{CONH2}	276.97 (0.018)	278.07 (0.006)	290.45 (0.005)	304.80 (0.001)	314.82 (0.001)	346.57 (0.001)
1_{CN}	221.75 (0.717)	239.90 (0.066)	243.74 (0.000)	246.84 (0.000)	304.65 (0.007)	325.03 (0.000)
1_{OH}	258.21 (0.001)	265.77 (0.001)	271.91 (0.000)	289.82 (0.000)	325.98 (0.000)	343.20 (0.001)
1_{NH2}	310.64 (0.003)	325.15 (0.010)	342.05 (0.002)	366.36 (0.000)	413.11 (0.001)	433.65 (0.015)
1_{CO2H-OH}	261.40 (0.005)	262.20 (0.002)	269.05 (0.040)	280.10 (0.006)	281.42 (0.001)	536.79 (0.004)
1_{NO2-NH2}	301.47 (0.007)	323.95 (0.018)	343.17 (0.002)	355.38 (0.043)	472.98 (0.013)	568.79 (0.053)
1_{CONH2-OH}	255.92 (0.013)	258.51 (0.001)	283.43 (0.001)	290.36 (0.002)	303.89 (0.015)	471.43 (0.000)
1_{CN-NH2}	257.32 (0.050)	259.37 (0.021)	276.84 (0.001)	283.55 (0.005)	342.62 (0.008)	611.42 (0.000)

withdrawing and electron donating substituents on the UV-visible absorption wavelength region were investigated on four positions of **1_x** (X attached at carbons C₂, C₃, C₅ and C₆) (Table-1). All the results of the UV-visible absorption wavelength region for both electron withdrawing and electron donating substituents at carbon atoms C₂, C₃, C₅ and C₆ of **1_x** were tabulated (Table-1).

In general, all the substituents change the spectral band position in the absorption, reflectance, transmittance, or emission spectrum of a molecule to a longer wavelength. Here, the electron donating and withdrawing substituents were selected for making higher efficiency of the **1_x/2_x** system in the absorption of UV-visible bands. Electron donating substituents (X = -NH₂ and -OH) of **1_x** absorb the UV-visible region light more than electron withdrawing groups (X = -NO₂, -CN, -CONH₂ and -CO₂H). The red shifts of the UV-visible absorption bands to the visible spectrum region through the electron withdrawing substituents are in the following order: **1_{NO2}** > **1_{CONH2}** > **1_{CN}** > **1_H**. The red shifts of the UV-visible absorption bands to the visible spectrum region through the electron donating substituents are in the following order: **1_{NH2}** > **1_{OH}** > **1_H**. The most efficiency of the UV-visible absorption among the substituents were belonged to **1_{NH2}**. At last, when both the electron donating and electron withdrawing substituents were attached at two sides of double bonds C₂=C₃ and C₅=C₆, absorb the visible region light more than the electron donating or electron withdrawing substituents. The red shifts of solar absorption bands to the visible spectrum region through the electron withdrawing-electron donating substituents were in the following order, respectively: **1_{NO2-NH2}** > **1_{CN-NH2}** > **1_{CO2H-OH}** > **1_{CONH2-OH}**. The solar absorption bands of **1_x**, shifted to the visible spectrum region, was mainly ascribed to the possibility of extension of conjugation of C=C by the attached substituents.

Conclusion

The effects of both electron withdrawing and electron donating substituents are investigated on various positions of **1_x** and **2_x**. The electron donating and electrons withdrawing substituents of **1_x**, attached at C₂, were suitable for the UV-visible absorption. The DFT calculations indicate that the solar absorption bands of **1_x** were shifted to the visible spectrum region through the electron withdrawing substituents more than through electron donating substituents.

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