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A Preliminary First Principle Study on Photochromism of Diarylethene Molecules

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ABSTRACT

Photochromism in some diarylethene molecules have been studied by using hybrid density functional theory using the ground state energy consideration. In particular, B3LYP functional and all electron basis set 6-311G (2d,2p) as implemented in Gaussian09 suites of program has been used to investigate the energy difference of two stable isomers of stilbene, azobenzene, cyclooctane, and 1,2, dimethylcyclohexane molecules. The energy difference is corroborated to calculate the frequencies of photons that are required to induce photochromism in these molecules in vacuum and in solvation state. The study found that the molecules exhibit photochromism at various frequency range from infra-red to ultraviolet. The binding energy per atom, charge distribution, HOMO-LUMO (Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital) gap are also calculated for all the molecules in vacuum, water and ethanol solvent. The results obtained are in accordance with the experimental observations.

KEYWORDS: Photochromism, DFT, Diarylethene, Gaussian09

INTRODUCTION

Photochromism originates from two words- photos and chroma. Etymologically, it means the property that undergoes light induced alteration of certain properties (Stevenson, 2010; Bouas-Laurent, 2001). The property of photochromism is very interesting because of the speed and accuracy. The speed of light being very high, any alteration in the properties induced by light is also very fast. If the response of the molecule is fast enough the phenomenon of photochromism can be implemented in myriads of applications such as storage of big data, process them to retrieve, extrapolate and interpolate to predict complex phenomena of social and scientific importance. Also, it is important to note that such phenomena can be modulated to a very long distance with the speed of light with unlimited energy supply. Moreover, if this property is reversible it can find applications in switches in macro to molecular scale. It has already found commercial applications in glass lenses, cosmetics, clothes, etc. (Higgins, 2003). For example, photochromism has been applied to manufacture lipsticks that can change color with the variation of intensity of ambient light (Simon & Bin, 2004).

There has been a significant interest in photochromism from the community of researchers in fluorescence microscopy imaging in the field of biology, medicine, material science, etc. (Nakatani, Piard, Yu, & Métivier, 2016). Photochromism can be implemented to develop faster microscopes with better resolutions. The optical resolution of conventional microscopes limited by fundamental diffraction limit can be improved with the implementation of photochromism.

Read write speed of data on CD and DVD are primarily optical phenomena (Szaciłowski, 2008). In those storage devices photons read and write information. This can be linked with photochromism. The process of writing, retrieving, erasing, and rewriting is reversible. If we can link the phenomena of photochromism with such reversibility, its application in the field of information technology is unbound. Advancement in nanotechnology has made possible the miniaturization of devices used in information technology, biomedicines, etc., with much increased efficiency and accuracy. The fundamental processes in nature are now understood not only at nanoscale level, but also at molecular level. There has been a growing concern on development of electronic devices based on manipulation of circuits at molecular scales. Such molecular devices have proven to be superior in speed and capacity of performance as compared to their macroscopic counterpart. They are found to be capable of rectification, memory storage, drug delivery, toxic gas detection, switching etc. (Kudernac et al., 2013). However, the integration of the various components of molecular devices is still difficult and challenging. Through understanding of underlying principles individual molecular component is crucial for development of such integrated systems of molecular devices. One of the most important aspect in this areas is to understand the nature of interaction of light with various component of molecular electronic circuit.

Molecular switches, in particular, light driven molecular switches have grabbed much attention in nanoscience community in recent decades (Zhang et al., 2015). Since light absorption and emission processes are extremely fast at electronic levels, response of light driven molecular switches is also very fast. Light can not only alter the electronic structure of molecules, but also can alter its geometrical structure. This alteration of geometrical structure can also be utilized for data storage if it is reversible. Incident light can be easily modulated to achieve desired outcomes from the selected molecule for switch. These promising features of light driven molecular switches with added advantage of miniaturization can have direct impact on molecular electronics engineering. Such a phenomenon of reversible transformation of electronic and geometrical structures due to exposure of light is called photochromism and has been manifested by some molecules such as Diarylethene (Irie, 2000). The current work investigates such molecules for possible application in molecular electronic devices.

Literature Review

The earliest reference of the phenomena of photochromism can be found in account of era of the Alexander (356-323 BC), the king of Macedonia in his conquest, he employed head warriors equipped with some kind of photochromic bracelets, unknown till date exhibiting to color change when exposed to sunlight. Such color change was used by the warriors to indicate the right moment to begin the battle (Dessauer & Paris, 1963). In 1867, an account of alteration of color of a molecule and its reversibility was reported by Fritzsche (Fritzsche, 1867). The first ever reported detail scientific work on photochromic organic compound at solid state is on 2,3,4,4-tetrachloronaphthalen-1-(4H)-one in 1899 by Markwald (Dürr & Bouas-Laurent, 2003). The field of research in photochromism got a real scientific traction after 1950s. The advancement of characterization techniques was crucial for synthesis and study of new photochromic

molecules. The word “photochromism” had become quite usual during 1950s and 1960s. Many new molecules were synthesized and studied during this period (Nakatani, Piard, Yu, & Métivier, 2016; Dessauer & Paris, 1963; Brown & Shaw, 1961; Cohen & Newman, 1967).

There has been an explosive growth of scientific research interest in fabrication and studies of photochromic molecules since last couple of decades (Zhang et al., 2015; Pathem et al., 2013; Jia et al., 2016) due to their fascinating physical, chemical, and optical properties and huge potential applications in the nano-electronics industry. Diarylethene is one of the most studied photochromic compound for molecular switches in the current literature (Irie, 2000; Feringa & Browne, 2001).

Diarylethene molecules are remarkable photochromic molecules that can respond to light and interchange their structure between two stable states reversibly (Kudernac et al., 2013). Figure 1 shows a schematic model of photochromism in stilbene, one of the simplest diarylethene molecules. The process of isomerization of molecules in presence of light can be used in molecular switches in nanoelectronics circuits. The compounds are remarkably resilient to elastic fatigue. They can undergo 10^4 cycles of deformation and reformation without showing any sign of fatigues (Irie, 2000). This property can be harnessed for optical control of structure and functionality with light. Masahiro Irie (2000) has calculated thermal stability, fatigue resistance, quantum yield and switching and memory relevant properties of these molecules and shown that the crystalline and amorphous diarylethene are of great promise in potential applications to memories and switches. Despite their huge potential applications, there are very few studies that have demonstrated bidirectional conductance switching. Jia et al. (2016) have demonstrated the use of single diarylethene molecule for a reversible molecular electrical switch in a graphene electrode junction. One of the most important challenge in realizing their practical commercial use is to make them work in a wide range of temperature (Dulić et al., 2007). To understand their temperature response, it is crucial to understand the potential barriers between ring opening and closing in these molecules under light (Nakamura & Irie, 1988). Therefore, the electronic structure calculations of these molecules under various conditions is desirable.

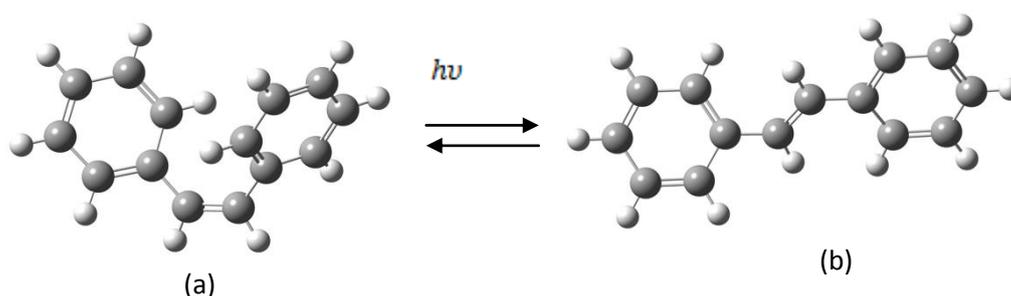


Figure 1: Photochromism in Stilbene molecule. (a) cis-stilbene (b) trans-stilbene. Grey spheres represent hydrogen atoms and black spheres represent carbon atoms.

The current research is a first principle investigation of diarylethene molecules under structural transformation during the switching process, i.e. the process of opening and closing of rings in the molecule under influence of electromagnetic radiation. The first principle calculations of these molecules will calculate their frontier orbitals, gap between frontier orbitals, structural stability under deformation, and their vibration states.

The study aims to elucidate the underlying principle of switching process of diarylethene molecules and direct toward the molecular engineering of photochromic molecules in general, diarylethene in particular. There are numerous research works on experimental aspects of these molecule, however to achieve a controlled molecular engineering, first principle electronic structure calculations required to understand the fundamental physics behind the switching process between two or more than two stable structures of the molecules. The work aims to shed light on experimental observations with electronic structure calculations and pathways to improve the efficiency these molecules in nano-electronic circuits.

Research Method

In this work, hybrid density functional theory incorporating Hartree–Fock (HF) exchange (Hehere et al., 1986) with density functional theory (DFT) exchange–correlation (Perdew et al., 1982) is being used to calculate the electronic and geometric structure properties of the diarylethene molecule. In particular, the work will use Becke’s three parameter exchange correlation functional mixed with Lee Yang Parr correlation functional, called B3LYP hybrid functional and the all-electron basis set 6-311G(2d,2p) as implemented in the GAUSSIAN 09 suite of programs (Frisch et al., 2009) for full geometry optimizations without any symmetry constraints of the diarylethene molecule structure. Figure 3 shows a flowchart of DFT calculations.

The accuracy of the employed functionals and basis sets were checked against the available experimental values available and relevant parameters of the molecules as discussed in the next chapter. Four molecules that have demonstrated the photochromism has been selected for this study. The molecules are stilbene, azobenzene, cyclooctane, 1, 2, dimethylcyclohexane are selected for the detail investigation in this study. All these molecules have stereoisomers which are interchangeable into each-other in presence of light as shown schematically in Figure 2. Trans-1,2-diphenylethylene, also known as trans-stilbene and cis-1,2-diphenylethylene, also known as cis-stilbene are the two isomers of stilbene. The cis-1,2-diphenylethylene higher energy than that of trans-1,2-diphenylethylene, i.e. the cis-stilbene is less stable than trans-stilbene. The energy difference is first needed to look for the suitable photon which can cause the cis-stilbene to trans-stilbene.

Results and Discussions

To check the validity of the method being implemented, the bond length of some dimers that are prevalent in the molecule were calculated. The B3LYP functional and 6-311G(2d,2p) calculated value of CH dimer CC dimer are 1.13 Angstrom and 1.26 Angstrom, which are comparable with the experimental values 1.09 Angstrom and 1.35 Angstrom respectively. Hence the basis set chosen and the functional is reliable enough for the purpose.

The functional B3LYP and basis set 6-311G(2d,2p) were used to optimize the trans- and cis-stereoisomer of all the molecules. The calculations were performed in vacuum state and solvation state in water and ethanol. Experimental geometry of the molecules were first obtained from ChemSpider, an open source database of molecules maintained and owned by Royal Society of Chemistry (Pence & Williams, 2010), and then optimized without any symmetry constraints. To check the relative stability of the molecules, the binding energy per atom were calculated.

Table 1. Stability of photochromic molecules in their two types in terms of binding energies per atom (in eV)

Molecules	Types	Energy (a.u)	B.E./atom (eV)
Stilbene	trans	-540.8136	6.01
	cis	-540.8037	6.00
Azobenzene	trans	-572.8694	6.11
	cis	-572.8565	6.10
Cyclooctane	trans	-313.2561	3.30
	cis	-313.3405	3.40
1,2, dimethylcyclohexane	trans	-314.6022	4.83
	cis	-314.5999	4.82

As it is evident from Table 1, all the molecules under study are stable with binding energies per atom ranging from 3.30 eV to 6.11 eV. The most stable of all the molecules, cyclo-octane in trans state is least stable and the azobenzene in trans state is the most stable. All the molecules except the cyclo-octane are more stable in their trans state than in their cis state.

Some prominent characteristics of some diarylethane molecules in trans and cis state such as energy, energy gap, dipole moment and HOMO-LUMO gap are explained here in vacuum are shown in Table 2. From the table, it is clear that cis-Stilbene has more energy than trans-stilbene. Also the dipole moment of trans-stilbene is greater than that of the cis-stilbene. The energy gap of the trans and cis- stilbene is 0.0098 eV. The HOMO-LUMO gap for the trans and cis stilbene are 0.144 eV and 0.163 eV. Trans-stilbene has less energy state than cis-stilbene therefore it is more stable because of its lower energy. For the azobenzene, trans-azobenzene has less energy than the cis-azobenzene, so trans-state is more stable than that of the cis azobenzene. They have the energy gap of 0.0129 eV. Cis-azobenzene has more dipole moment than that of trans-azobenzene. The HOMO-LUMO gap for cis azobenzene is found to be greater than that of the trans-azobenzene. Having less energy trans state of azobenzene is more stable than cis state.

Similarly for the cyclooctane molecule, cis-cyclooctane has less energy than that of the trans-cyclooctane so cis-state is more stable than trans-state. They have a little bit more energy gap 0.0844eV. Trans-cyclooctane has more dipole moment than that of the cis cyclooctane. HOMO-LUMO gap of cis cyclooctane is greater than that of the trans-cyclooctane. Cis-cyclooctane is more stable than trans -cyclooctane. In case of dimethylcyclohexane molecule, cis state has lower energy than that of trans- state of molecule so cis- is more stable than that of the trans state. The dipole moment of trans-state is greater than that of cis- state of the molecule. HOMO-LUMO gap for trans is found to be greater than that of the cis- state.

Table 2. Calculation of energy of molecules (in vacuum)

S.N	Molecules	Types	Energy (in a.u)	Dipole moment (debye)	HOMO-LUMO gap(ev)	ΔE (au)
1.	Stilbene	trans	-540.813	0.050	0.144	-0.0098
		cis	-540.804	0.159	0.163	

2.	Azobenzene	trans	-572.869	0.106	0.103	-0.0129
		cis	-572.856	2.915	0.106	
3.	Cyclooctane	trans	-313.256	0.268	0.208	-0.0844
		cis	-313.340	0.254	0.246	
4.	1,2, dimethylcyclohexan e	trans	-314.600	0.137	0.330	-0.0023
		cis	-314.602	0.071	0.321	

Table 3 : Calculation of energy of molecules with water solvent

S.N	Molecules	Types	Energy (in a.u)	HOMO-LUMO gap (ev)	ΔE
1.	Stilbene	trans	-540.819	0.144	-0.0107
		cis	-540.808	0.164	
2.	Azobenzene	trans	-572.875	0.107	-0.0111
		cis	-572.864	0.109	
3.	Cyclooctane	trans	-313.258	0.205	0.0837
		cis	-313.341	0.224	
4.	1,2, dimethylcyclohexane	trans	-314.603	0.331	-0.0024
		cis	-314.600	0.322	

Table 4 : Calculation of energy of molecules with ethanol solvent

S.N	Molecules	Types	Energy (in a.u)	Dipole moment (debye)	HOMO- LUMO gap(ev)	ΔE
1.	Stilbene	trans	-540.819	0.077	0.144	-0.0107
		cis	-540.808	0.084	0.164	
2.	Azobenzene	trans	-572.875	0.144	0.107	-0.0112
		cis	-572.864	3.984	0.109	
3.	Cycloocten	trans	-	0.389	0.208	0.0837
		cis	313.2578 -313.341	0.372	0.247	
4.	1,2, dimethylcyclohexane	trans	-314.602	0.084	0.331	-0.0024
		cis	-314.600	0.171	0.311	

It is seen (Table 3) that trans-stilbene in water has less energy than that of the cis-stilbene so trans state is more stable than cis state. Also HOMO-LUMO gap of cis state is more than that of the trans state. The energy gap of trans and cis states of stilbene is found to be 0.0107 au.

For the Azobenzene in water trans-state energy is less than that of the cis state energy so trans state is more stable than that of the cis state. The HOMO-LUMO gap of cis state is slightly greater than that of the trans state. The energy gap of those trans and cis states is 0.0111 au.

Likewise for the cyclooctane molecule cis state has less energy than that of the trans state so cis cyclooctane is more stable than that of the trans-cyclooctane. The HOMO_LUMO gap of cis cyclooctane is greater than that of the trans cyclooctane. They have the energy gap of 0,0837 eV.

Finally for dimethylcyclohexane, trans state has slightly less energy than that of the cis state. So trans-dimethylcyclohexane is more stable than cis state. Also HOMO-LUMO energy gap of trans state is more than that of the cis state. The energy gap of trans and cis state is 0.0024 eV.

Trans-stilbene in ethanol has less energy than that of cis stilbene in ethanol, so trans-stilbene is more stable than cis stilbene. Hence we can say that trans-stilbene is more stable than cis stilbene. Dipole moment in cis state is greater than that of the trans state. The HOMO-LUMO gap of cis is greater than that of the trans state. They have the energy gap of 0.0107 au.

Also trans Azo benzene in methanol has less energy than that of the cis-azobenzene, so trans-state is more stable than that of the cis state. Dipole moment of cis state is much greater than that of the trans-state. The HOMO-LUMO gap of cis state is greater than that of the trans state. They have significant energy gap of 0.0112 au.

Likewise, for cyclooctane molecule cis state has less energy than that of the trans state so cis state is more stable than trans state of cyclooctane molecule in ethanol. Also the dipole moment of trans cyclooctane in ethanol is greater than in the cis state of the cyclooctane in ethanol. The HOMO-LUMO gap for cis cyclooctane is greater than that of the trans cyclooctane in ethanol. The energy gap of trans and cis state is 0.0837 au which is significantly high.

For the dimethylcyclohexane in ethanol the molecule in trans state has slightly smaller energy than that of the cis state of the same molecule so trans –state of the molecule is more stable than that of the state of the same molecule. Dipole moment of cis state is almost double than that of the trans state of the same molecule. The HOMO-LUMO gap for trans state is greater than that of the cis state of the molecule. The energy gap of trans and cis state of the same molecule in ethanol is found to be 0.0024 au.

Table 5: Frequency of radiation that will induce photochromism of molecules

S.N.	Names of molecules	Frequency(Hz)		
		Vacuum	Water	Ethanol
1	Stilbene	6.477×10^{13}	7.038×10^{13}	7.020×10^{13}
2	Azobenzene	8.463×10^{13}	7.302×10^{13}	7.340×10^{13}
3	Cycloocten	5.552×10^{14}	5.504×10^{14}	5.505×10^{14}
4	1,2,dimethylcyclohexane	1.547×10^{13}	1.552×10^{13}	1.552×10^{13}

Table 5 summarizes the photochromism in the molecules under study in terms of the frequency of radiation that would induce photochromism in the molecules. It is found that photochromism in stilbene in vacuum is achieved by the photons of frequencies 6.477×10^{13} Hz which is the photons of blue light. Hence blue light can induce photochromism for stilbene molecules in vacuum. Also photochromism of stilbene molecules in water is achieved by the photons of frequencies 7.038×10^{13} Hz which corresponds to the photons of violet light. Hence violet light can induce photochromism for stilbene molecules in water. Photochromism of stilbene molecules in ethanol is achieved by the photons of frequencies 7.020×10^{13} Hz, which are the photons of violet light. Hence the violet colored lights shows photochromism for stilbene molecules in ethanol. It shows that more energetic photons are required for photochromism in water than that of vacuum. But for ethanol even the photons of slightly smaller energy than that of waters can induce photochromism in stilbene molecules. For Azobenzene molecules in vacuum photochromism can be induced by the photons of frequencies 8.463×10^{13} Hz which are

the photons of ultraviolet light. Hence ultraviolet light can induce photochromism of azobenzene molecules in vacuum. But photochromism of azobenzene molecules in water is achieved by the photons of frequencies 7.302×10^{13} Hz which are the photons of violet light. Hence violet light can induce photochromism of azobenzene molecule in water. Also, photochromism for azobenzene molecule in ethanol is obtained by the photons of frequencies 7.340×10^{13} Hz which are also the photons of violet light.

It is found that more energetic photons are required for photochromism in vacuum than in water for azobenzene molecules. But for ethanol molecules less stronger photons than that of the ethanol but stronger than that of water are required for photochromism. For cyclooctane molecules in vacuum photochromism can be induced by the photons of frequencies 5.552×10^{14} Hz which are the photons of ultraviolet light. Hence ultraviolet light can induce photochromism of cyclooctane molecule in vacuum. But photochromism of cyclooctane molecule in water is achieved by the frequencies 5.504×10^{14} Hz which are also the photons of ultraviolet light. Also, photochromism for cyclooctane molecules in ethanol is obtained by the photons of frequencies of 5.505×10^{14} Hz which are also the photons of ultraviolet light. It is calculated that more energetic photons are required to induce photochromism for cyclooctane molecules in vacuum than that of water where for ethanol it is almost equal to that of the water.

For dimethylcyclohexane molecules in vacuum photochromism can be induced by the photons of frequencies 1.547×10^{13} Hz, which are the photons of infrared radiations. Hence infrared radiations can induce photochromism of dimethylcyclohexane molecules in vacuum. But photochromism of dimethylcyclohexane molecules in water can be induced by the photons of frequencies 1.552×10^{13} Hz, which also corresponds to the photons in infrared region. Hence infrared radiations can induce photochromism of dimethylcyclohexane molecules in water. Also, photochromism of dimethylcyclohexane molecules in ethanol is obtained by the photons of frequencies 1.552×10^{13} Hz which corresponds to the photons in infrared region. Hence the same infrared radiations can induce photochromism of dimethylcyclohexane molecule in ethanol. It shows that more energetic photons are required for photochromism of dimethylcyclohexane molecules in vacuum than in water and ethanol. Hence, we observed that dimethylcyclohexane in water and ethanol get induced by the photons of equal energies. The transition of molecules from one state to another are summarized the Figures 3-18.

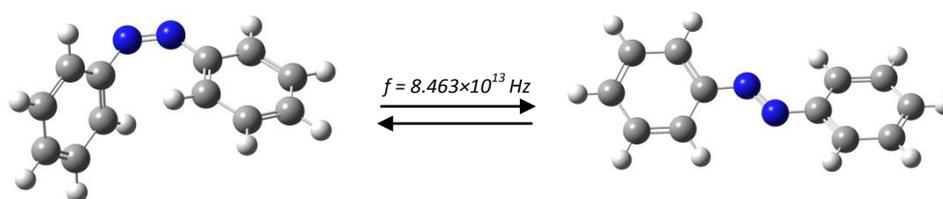


Figure 4. Photochromism of azobenzene under the radiation of frequency $f = 8.463 \times 10^{13}$ Hz. Blue spheres represent nitrogen atoms, grey sphere represent carbon atoms and white spheres represent hydrogen atoms.

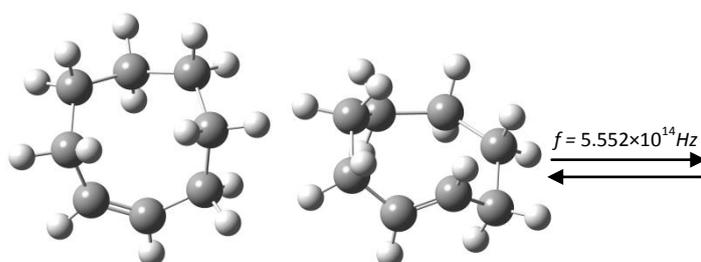


Figure 8. Photochromism of cyclooctane under the radiation of frequency $f = 5.552 \times 10^{14} \text{ Hz}$. Grey sphere represent carbon atoms and white spheres represent hydrogen atoms.

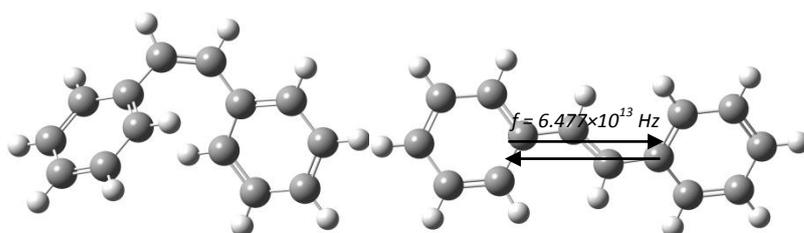


Figure 12. Photochromism of stilbene under the radiation of frequency $f = 6.477 \times 10^{13} \text{ Hz}$. Grey sphere represent carbon atoms and white spheres represent hydrogen atoms.

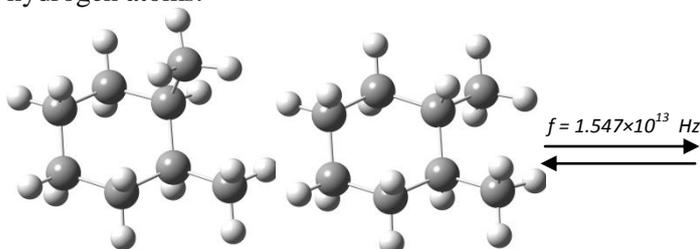


Figure 16. Photochromism of 1,2, dimethylcyclohexane under the radiation of frequency $f = 1.547 \times 10^{13} \text{ Hz}$. Grey sphere represent carbon atoms and white spheres represent hydrogen atoms.

CONCLUSIONS

From the electronic structure calculations with hybrid DFT, it is established that the molecules stilbene, azobenzene, cyclooctane, 1,2, dimethylcyclohexane can be interchanged from their one state to another by photons of varying frequencies. The frequencies of photons that can induce photochromism depends not only on the structure of the molecules but also on the solvation. For example, the molecule azobenzene can show photochromism at a frequency of $8.5 \times 10^{13} \text{ Hz}$ in vacuum whereas the same molecule can show photochromism at frequency of $7.3 \times 10^{13} \text{ Hz}$ in water solvent. Similar behavior is shown by all the molecules. However, the order of magnitude of the frequency is not quite different in solvation states. The calculation and the conclusions drawn in the study are based only on the ground state energies at absolute zero temperature. However, the photochromism can be affected by the excited states of the molecules and thermal vibrations of the molecules.

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