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Study of Photoisomerization in Cis-Retinal as a Natural Photo switch in Vision Using Density Functional Theory

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ABSTRACT

In the present study, theoretical chemical reactivates Photo isomerization in Cis-Retinal as a Natural Photo switch in Vision. DFT hybrid functional, B3LYP and, post-HF method, were the theoretical methods applied utilizing G09 software. 6-31G+ (d,p) basis set employed for structural optimizations, and single point computations performed using B3LYP/6-31G+(d,p). The isomers cis molecule retinal from 0 to 180 ° in steps of 10 degrees to the trans isomers convert and we calculate the energy in each step, we determined that the most appropriate angle for the conversion of isomers of cis to trans angleθ = 90.11 ° the energy barrier less be.It identified that transmission S0→ S1 is the most likely transmission.

Key words: Photoisomerization, Retinal, Photo switch, DFT, B3LYP

INTRODUCTION

The mechanism of vision is present in most living creatures (Hargrave et al., 1983). In animals this mechanism is supported by a complex apparatus, but the ability to transform external optical perturbations in chemical signals is also present in the most primitive formsof life such as bacteria (Meyer, 1987). In all cases the first and most important step of the mechanism is the photoisomerization of the rhodopsin chromophore. Upon the absorption of a photon, its geometrical con-formation changes from 11-cisto all-trans by a rotation along theaxis connecting two carbon atoms of the polyenic chain (C11 andC12, see Figure 1).

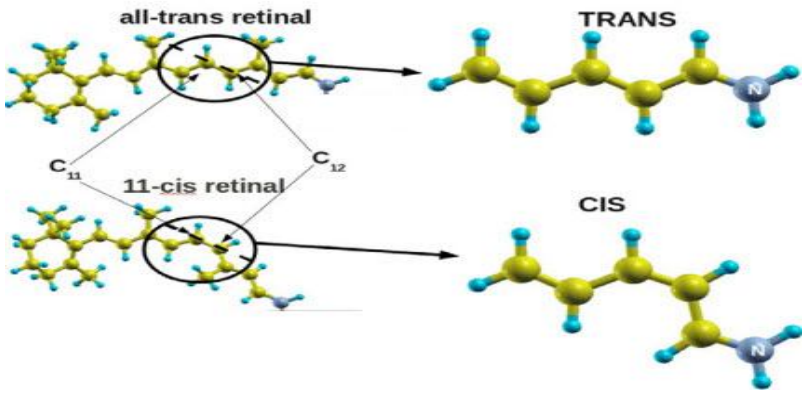

Figure 1. All-trans retinal and 11-cis retinal.Dashed lines

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Indicate the rotation axis during the isomerization process Despite the importance of this process andseveral experimental (Kukura., 2005) and theoretical studies (Valsson, 2010). On this topic, the photoisomerizationmechanism is not yet fully understood (Nielsen, 2006). A theoretical description and evaluation of the efficiency andvelocity of the photoisomerization of the 11-cisretinal is possible only by a very precise calculation ofthe excited-state energies along all the phases of the isomerization. This study attempts to investigate the exact reaction pathway and to answer the question of howmany excited electronic states are involved in the internal conversion process as well as to calculate the energetics of the initial step of cis–transtrans formation for the photoisomerization of the retinal chromophore.Vision is a complex process in which light is converted into a nervous impulse through a chain of biochemical reactions taking place along various specialized cells and tissues, from the retina of the eye to the brain. In the eye, specialized cells of the retina called rod cells contain a protein acting as a photoreceptor, rhodopsin and possess the unique ability to convert and generate the neuronal signal. In order to become activated and induce the enzymatic cascade leading to vision (Albert, 2002) rhodopsin relies on its chromophore, retinal (Hofmann KP. 2000). Retinal is an organicmolecule (Figure 2) covalently-bound to rhodopsin in anticipation of its photo-activationThe 11-cis-retinal isomer is a key photosensitive component of rhodopsin. It is a molecular trigger capable of converting the electromagnetic energy carried by a photon into mechanical energy to be transferred to the protein in order to induce slower conformational changes, eventually leading to the initialization of the chain of biochemical reactions leading and finally to neural signal (Sakmar,1998). To perform its function, 11-cis-retinal undergoes a fast photoisomerization leading to all-trans-retinal,a process which triggers the conformational changes of the receptor to its active form (metarhodopsin II) (Yoshizawa T 1963).

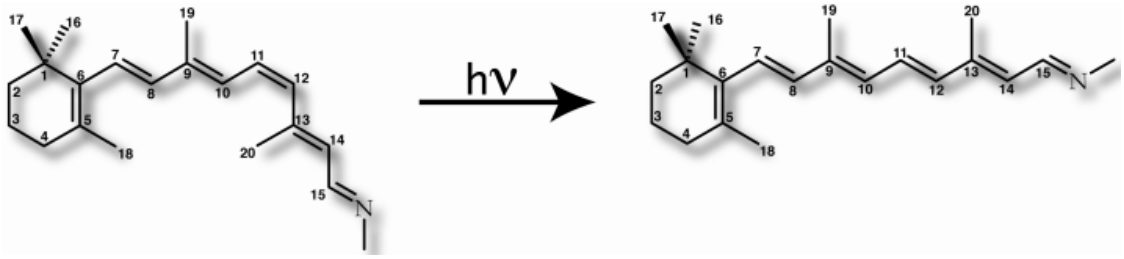

Figure 2.Chemical structure of 11-cis-retinal and all-trans-retinal.

Computational methods

In order to study photoreactions we need amethodology to deal with excited states. Densityfunctional theory (DFT) has proved to be a verysuccessful tool for describing ground state prop-erties of systems of chemical and materials scienceinterest (Parrinello, 1998). Extending DFT to deal with excitedstates, still preserving its favorable ratio between accuracy and computational cost, is an extremelyimportant step that would open the path to thestudy of interesting photo processes. Although various DFT-based methods for excited stateshave been proposed and often quite successfullyapplied to the calculation of vertical excitationenergies (Singh 1999), the problemof moving on excited state potential energy surfaces, to perform geometry optimization or mo-lecular dynamics, remains a major challenge. In this work we study the photoisomerization in Cis-Retinal by Density Functional Theory (DFT).The B3LYP/6-31+G (d,p) electronic structure methods are employed to calculate the energies of the four lowest lying singletstates as a function of the reaction coordinate. One dimensional potential energy curves for the isomerization of retinal, i.e., isomerization from C11=C12cis-forms to trans forms, have been calculated by means of time-dependent density functional theory (TD-DFT) calculations to elucidate the mechanism of initial step in photo absorption. We calculated the ground-state and excited-state energy of retinal

correspond respectively to a rotation around the main molecular axis of about (0°,10°,20°,…,180°), (table 1, table 2).For the potential energy surface of both the ground and excited state, the rotation about the C11 –C12 bond, characterized by the twist angle θ(C10 –C11 –C12 –C13), is considered.

Table1. Energy Specifications of the ground state

Change angle	Energy(ev)
0	-23035.96
10	-23035.96
20	-23035.98
30	-23035.99
40	-23035.91
50	-23035.72
60	-23035.74
70	-23034.97
80	-23034.47
90	-23034.00
100	-23034.50
110	-23035.00
120	-23035.44
130	-23035.85
140	-23036.21
150	-23036.49
160	-23036.71
170	-23036.82
180	-23036.88

Table2. Energy Specifications and wave length thefirstexcitation

Singlet Change angle	(ev)Energy	Excitation wavelength(nm)
0	3.01	411.49
10	2.99	414.06
20	2.94	420.85
30	2.86	433.07
40	2.73	454.12
50	2.52	490.80
60	2.22	558.11
70	1.78	693.86
80	1.19	1041.52
90	0.11	1079.53
100	1.21	1018.14
110	1.81	681.58
120	2.26	547.83
130	2.57	481.38
140	2.78	445.69
150	2.91	425.61
160	2.99	414.24
170	3.03	408.44
180	3.04	406.85

Results and discussion

The obtained result revealed that transition state of the isomerization in the first excited state is best located at θ11–12=90.11, where θ11–12 means twist angle around the C11=C12 double bond of retinal. At this angle, the potential barrier is formed by the avoided crossing between S0 and S1 states. The mechanism of the isomerization was discussed on the basis of theoretical results(Figure 3).Calculations of energies and geometries forboth vertical and adiabatic excitations for a seriesof unsaturated compounds have shown good accuracy compared to experiments and more sophisticated multi reference calculations.

As is thecase for time-dependent DFT calculations, excitation energies are underestimated. Rhodopsin and bacteriorhodopsin have beenextensively investigated. Many calculations usingforce-field, (Humphrey 1994)semi empirical(Warshel, 1976)and ab initio methods, (Vreven 1997) and alsocombined classical/quantum mechanical simulations, applied to more or less complexmodels, have been performed; the references citedhere represent a selection from the huge literatureon the subject. However, there are still many openquestions in understanding the photoreaction details.

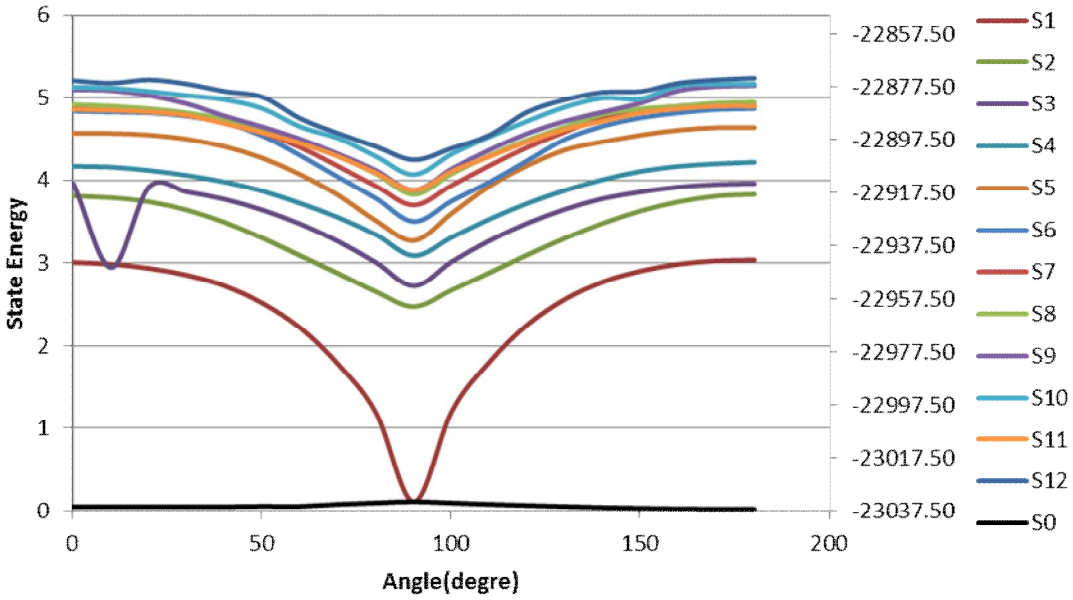

Figure3. Energydiagram ofthe changemodesdepending onthe degree

In particular, the C11-C12 bond length increases considerably making it a favorite candidate for the isomerisation. When the isomerisation is forced by constraining s, the C11-C12 bond increases in length, completely losing its original double bond character, which is fi nally regained in the trans form, as shown in Figure. 4.

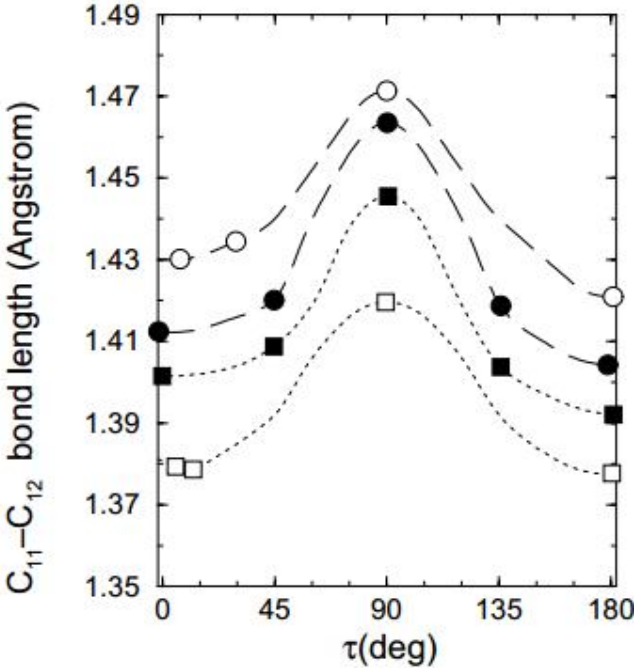

Figure.4. C11-C12 bond length as a function of the torsional angle τ for the protonated Schiff base of retinal without (filled symbols) and with the countering group and water molecule (empty symbols) in the ground (squares) and excited (circles) states.

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