



Density functional theory study of linear and non-linear optical properties of dihydroazulene-vinylheptafulvene photoswitches



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ABSTRACT

The UV–vis absorption spectra and hyperpolarizability of a series of substituted dihydroazulenes (DHAs) and vinylheptafulvenes (VHFs) photochrome are studied at B3LYP/6-31G(d,p) level of theory. Electronic properties strongly depended on the nature and position of substituents on DHA-VHF photoswitch. Electron withdrawing groups (NO₂, CHO) and halogens at position 8a of DHA cause red shift of the λ_{\max} , whereas blue shift of λ_{\max} was observed when these functional groups were present at positions 8, 7, 5 and 4. Mesomerically electron donating groups (NH₂, OH, and SH) on DHA cause hypsochromic shift of the λ_{\max} except amino and thiol at positions 4 and 6 (Red shift of λ_{\max}). The absorptions maximum of VHF, on the other hand, was red shifted for any functionalization at the seven membered ring of VHF. The maximum red shift of λ_{\max} (VHF) was observed for substituents at positions 8a, followed by position 6 and 4. Electron donating substituents are very effective at decreasing the spectral overlap of DHA and VHF. In general, hyperpolarizabilities of VHFs are higher than their corresponding DHAs. For electron withdrawing groups, the largest β (8.80 esu) was obtained for DHA bearing NO₂ at position 6. Among electron donors, NH₂ substituted DHAs showed the higher β values compared to the molecules bearing OH and CH₃. For VHF, the highest value of β (16.58 esu) was observed for molecule bearing bromine at position 6.

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1. Introduction

Molecular photoswitches interconvert between two (or more) isomeric states by light of different wavelengths. Photoswitches find application in memory [1], electronic switches, magnetic switches [2–4], non-linear optics (NLO) [5,6], synthetic ion channels [7,8], biological systems, liquid crystals [1,9–19], and even more complex devices including logic gates, half adder [20–28] encoder-decoder [29]. For practical application in memory and other related non-linear optical devices, a photoswitch must have minimum overlap of absorption spectra of isomeric species, but the polarizability difference between isomeric states should be high. Overlap of absorption spectra of isomeric species leads to photostationary state formation where substantial amounts of both isomers exist, and the process is not complete on either side. Some other requirements for practical applications include; high thermal stability, fatigue resistance, non-destructive readout and high quantum yield of photochemical conversions [7].

The most commonly studied classes of photoswitches are dithienylethene [7] and fulgides [34], mainly because of the

associated thermal stabilities. A less explored, but potentially important class of photochromic compounds is dihydroazulene-vinylheptafulvene (Fig. 1). The colorless dihydroazulene (DHA) is thermodynamically more stable than the photogenerated colored vinylheptafulvene (VHF) [30–38]. The *s-cis* conformer of vinylheptafulvene, generated from photochemical process, is in equilibrium with relatively more stable *s-trans* conformer. The vinylheptafulvene returns back to dihydroazulene [31,33,34] either photochemically, or thermally (T-type photoswitch) [39]. Besides thermal instability of VHF form, synthetic challenges for this class of photoswitch provide another obstacle for application in practical devices.

The focus of research in DHA-VHF photoswitch had been two fold; (a) design of multimode photoswitches by fusing DHA-VHF photoswitch with dithienylethene [40], and other photochromic molecules (b) exploration of variation in physical properties through structural modifications [31–34,37,38]. The latter has been limited to functionalization at position 2 and 3 of DHA (five membered ring, Fig. 2), mainly because of the associated synthetic challenges for functionalization at other position. With the advent of modern synthetic strategies, it is now possible to functionalize [41–43] the seven membered ring of DHA.

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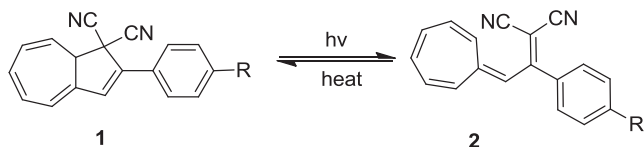


Fig. 1. Dihydroazulene vinylheptafulvene photoswitch (R = Ph).

Functionalization at the seven membered ring imparts very interesting properties to the dihydroazulene-vinylheptafulvene photoswitch. For example, Nielsen and coworkers reported that protonation of the amino group on the phenylethynyl DHA (**3**) shuts down the thermal return of VHF (**4**) to DHA (**3**) (Fig. 3). Inspired by this, we have recently started theoretical exploration of the properties of DHA-VHF through functionalization at the seven membered ring. Towards this end, we have studied the thermal reversion of a series of substituted VHF (at seven membered ring) to DHA [44]. Quite interesting trends in properties are predicted with variation in nature and position of functionalization. We have shown that the energy of activation for electrocyclization differs up to 7 kcal mol^{-1} with either change in the position or nature of functionalization. For example, 5-OH VHF (see Fig. 2 for numbering scheme) cyclizes thermally to DHA with an activation barrier of $23.74 \text{ kcal mol}^{-1}$, whereas the activation barrier for 4-OH VHF is $30.54 \text{ kcal mol}^{-1}$. On the other hand, an electron withdrawing formyl (CHO) group at position-5 of DHA-VHF pair imparts very high activation barrier for electrocyclization ($29.46 \text{ kcal mol}^{-1}$), compared to $23.74 \text{ kcal mol}^{-1}$ for 5-OH. Similarly, DHA-VHF photoswitch with an amino group at position 7 has relatively low activation barrier of $24.35 \text{ kcal mol}^{-1}$ whereas an electron withdrawing formyl (CHO) group imparts very high activation barrier ($31.29 \text{ kcal mol}^{-1}$). These findings are consistent with the earlier findings by Nielsen and coworkers. In the continuation of our ongoing studies on DHA-VHF photoswitch [44], we have carried out theoretical calculation to predict the effect of functionalization on the spectral and electronic properties.

The absorption spectrum of both isomers of a photoswitch pair should not overlap, in order to avoid photostationary mixture formation. DHA and VHF have different absorption spectra in UV-vis range of electromagnetic radiations; however the difference is not very large. For example, Phenyl substituted DHA (**1**) (R = H, Fig. 1) exhibits absorption maximum at 354 nm in toluene whereas the VHF isomer shows absorption maximum at 459 nm in the same solvent. The purpose of this study is to explore DHA-VHF photoswitches with more enhanced differences in absorption spectra. To the best of our knowledge, there is no existing detailed study on the effect of functionalization at the seven membered ring on the UV-vis absorption spectra of DHA/VHF photochrome. Moreover, hyperpolarizabilities are also studied because hyperpolarizability difference between two isomers should be large for practical application in NLO devices.

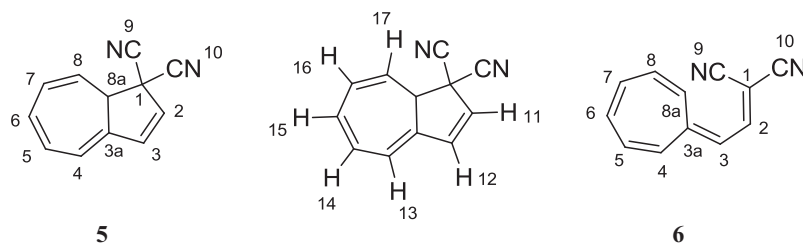


Fig. 2. Number scheme for discussion of simplified DHA and VHF.

2. Computational methods

All calculations were performed with Gaussian 09 [45]. Geometries of all structures were optimized without any symmetry constraints at PBE0/6-31G(d,p). The PBE0 method is cost effective and is known to perform very well to accurately predict the structural properties of organic dyes including DHA-VHF [44]. We have also shown in our recent report that the energies and geometries of DHA/VHF at PBE0 method correlate nicely with the experimental results [44]. Frequency calculations have also been performed at PBE0/6-31G(d,p) in order to confirm the structures as true minima (no imaginary frequency). The UV-vis spectra are modeled at TD-DFT method at B3LYP/6-31G(d,p) level of theory on PBE0/6-31G(d,p) optimized structures. The UV-vis spectra are modeled in the gas phase except for DHA (**1**) and VHF (**2**). The UV-vis spectra of **1** and **2** are calculated in THF solvent using polarization continuum model (PCM) to compare with the literature experimental values (in THF). The reported absorption maxima are absorption at maximum wavelength with oscillator strengths >0.2 . The hyperpolarizability values are also calculated at B3LYP/6-31G(d,p) level of theory because of the associated accuracy. The charge analysis was performed through Mulliken charge analysis scheme as implemented in Gaussian 09.

3. Results and discussion

3.1. UV-vis spectrum of unsubstituted DHA and VHF (experimental model)

A fundamental requirement of a photoswitch for practical applications is non-overlapped UV-vis spectra of both isomers. Overlapping of the absorption spectra generally results in the formation of a photostationary state upon photoisomerization. The ratio of constituents in the photostationary state depends on the region of irradiation, rate of thermal return reaction, time of irradiation as well the quantum yield of each isomer [46]. For DHA/VHF pair, an ideal substituent will be the one which imparts red and blue shifts to the absorption maxima of VHF and DHA, respectively.

Jacquemin and coworkers have discussed the electronic excitations and associated orbitals responsible for the UV-vis bands of DHA and VHF through calculations at CAM-B3LYP, PBE0 and wB97XD [47]. Experimental shift of the absorption maximum on transition from phenyl DHA (**1**) (354 nm) to VHF (**2**) (459 nm) is 105 nm; however, the calculated differences at CAM-B3LYP, PBE0 and wB97XD are 87, 87 and 90 nm, respectively. The above mentioned methods are quite good at predicting the absorption spectrum of VHF but, they give slightly deviated values for the absorption spectrum of DHA. We show here that B3LYP method, on the other hand, is quite reliable in predicting the absorption maximum of DHA. We have modeled the UV-vis spectrum of DHA (**1**) and VHF (**2**) in THF. The maximum of absorption spectrum of DHA is in full agreement with the experimental values (354 nm exp, 357 nm calc); however the calculated absorption of maximum

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