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Research Article

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Time Dependent Density Functional Study on the Electronic Spectra of Some Derivatives of Triafulvalene

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Abstract: Triafulvalene is a compound of immense theoretical applications, having a planar geometry of D_{2h} symmetry, with two three- member rings consisting of an endocyclic double bonds in each ring and an exocyclic double bond common to both rings. The paper presents the result of a theoretical study on the effect of functional groups on λ_{max} of triafulvalene. The molecules used in the study are triafulvalene, mono substituted triafulvalene where the substitutents are $-C_2H_4$, -CHO, -OH, -CN, $-NH_2$, $-NO_2$ and -Cl; di tri and tetra substituted fulvalenes, where the substituents are $-C_2H_4$ and $-NO_2$. The correlation between HOMO- LUMO gap and bond lengths with λ_{max} is analyzed in detail for vinyl and cyano substituents. Geometries are optimised using PBEPBE functional using 6-311++G (2d,p) basis sets and to generate the electronic energy states and UV- Visible data Time Dependent Density Functional Theory studies are performed using the same theoretical level. Studies shows that functionasl groups with multiple bonds increases the absorption maximum and in the case of multi substituted systems, the absorption maxima depends on the HOMO-LUMO gap.

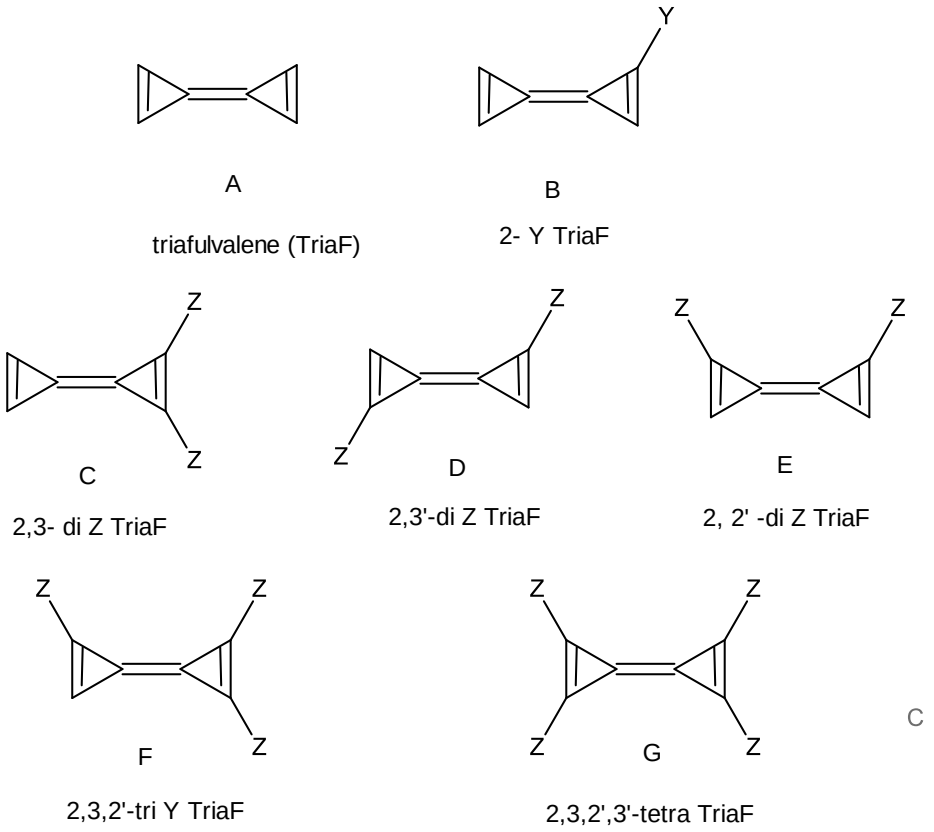
Keywords: TD-DFT, triafulvalene , HOMO-LUMO energy gap, UV-Visible Spectra

1. INTRODUCTION

The fulvalenes are generally a class of hydrocarbons which usually contain cross-conjugating two rings through a common exocyclic double bond [1]. The name is derived from the similarly structured fulvenes which lack one ring.

The lowest of its class, namely triafulvalene consists of two three member ring connected via a double bond with each ring having an endocyclic double bond [2]. Its inherent instability makes it difficult to synthesise; but several attempts are reported in the scientific literature [3–7]. But many analogues of other fulvalenes like pentafulvalene [8], diarylated dithienofulvalenes [9],

dibenzopentafulvalene [10], proaromatic electron receptor fulvalenes [11] are synthesised by benzanullation and substitution. Some members like



Scheme 1. Triafulvalene and their analogues

pentafulvalene are stabilised by a dipolar mesomeric form. Transition metal complexes of different fulvalenes were also reported [12,13].

This inherent instability and difficulty in synthesis subjected this class of compounds to immense theoretical studies. Computational analyses of triafulvalene shows a planar geometry, having D_{2h} symmetry. Theoretical studies on the ground state geometry of triafulvalenes and some of its analogues was reported in 1964 using PPP method [14]. Second [15] and third [16] hyper polarizabilities [14] of triafulvalenes and related compounds are also reported. Pseudo Jahn Teller distortion is observed in the anions of triafulvalene and fulvalenes [17] and also in the electronically excited states [18]. Aromatic stabilisation and anti-aromatic destabilisation of fulvalene class of compounds are also investigated to explain their stability and reactivity [19–22].

In this research, an attempt is made to study the effect of functional groups on λ_{max}, of triafulvalene and its some derivates, which are formed by replacing hydrogen(s) in triafulvalene (A) by Y and Z groups to get, mono substituted fulvalenes (B) (Y= –CH=CH_2, -CHO, -OH, -CN, -NH_2, -NO_2 and -Cl), di substituted fulvalenes (C, D and E) (Z=–CH=CH_2, and-NO_2), tri and tetra substituted forms (Z=–CH=CH_2, and-NO_2).

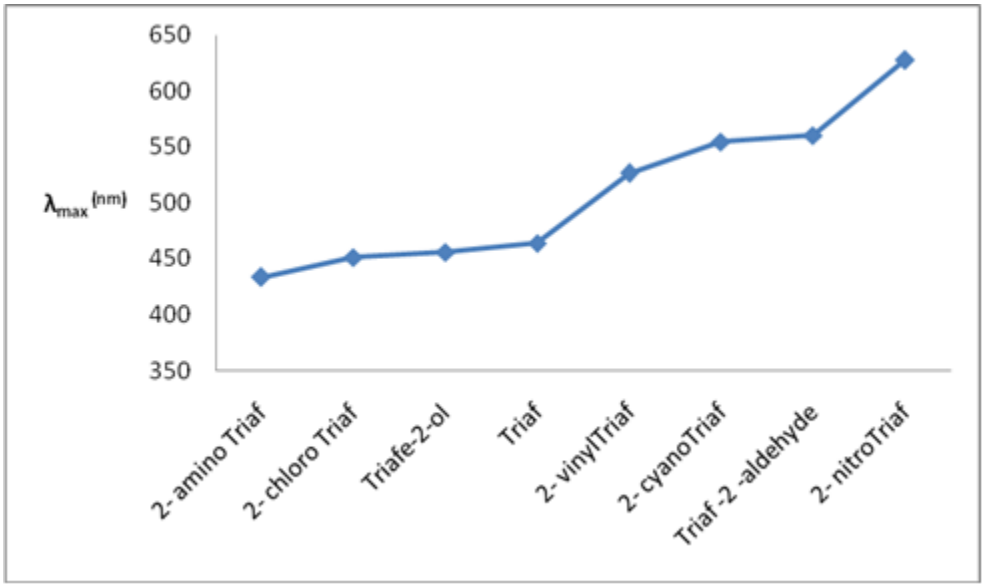


Figure 1. Variation of λ_{max} of different substituted triafulvalenes. All calculations performed using TD-DFT PBEPBE/6-311++G(2d,p). Values reported in nm.

2. MATERIALS AND METHODS

The molecules used in the present study are triafulvalene and their analogues (Scheme 1). Triafulvalene is a cyclic compound, which is formed as a result of joining two cyclopropenyl systems using a double bond. Even though it is having same number of carbon atoms and double bonds as the benzene molecule, they differ widely in their stability. No delocalisation of electrons has been observed in the case of triafulvalene, making it less stable then benzene.

To study the effect of functional groups on λ_{max} of triafulvalene, hydrogen was replaced by various substituent like $–CH=CH_2$, -CHO, -OH, -CN, $-NH_2$, $-NO_2$ and -Cl. The molecules used are triafulvalene (A), mono substituted fulvalenes (B) and disubstituted fulvalenes (C, D and E), tri substituted (F) and tetra substituted (G) where Y= $–CH=CH_2$, and -CN.

Theoretical studies of the UV- Visible spectra of above compounds are performed [23,24]. The geometries are optimized using PBEPBE level using 6-311++G(2d,p) basis set. The geometry thus obtained is used to generate UV-Visible spectra by Time Dependent Density Functional Theory (TD-DFT PBEPBE) method using the same basis set. Calculations are performed using Gaussian 09W [25] software.

3. RESULTS AND DISCUSSIONS

The energy of triafulvalene found as a result of PBEPBE/6-311++G(2d,p) is -230.56514173 a.u. Benzene, which has a similar molecular formula, is found to have energy of -232.00017468 a.u. This shows that triafulvalene is unstable than benzene by an amount of 1.43503295 a.u. Literature shows that

benzene is aromatic whereas triafulvalene is non aromatic. Thus triafulvalene is a typical unstable system as the electrons are not delocalised which is evident from the energy values.

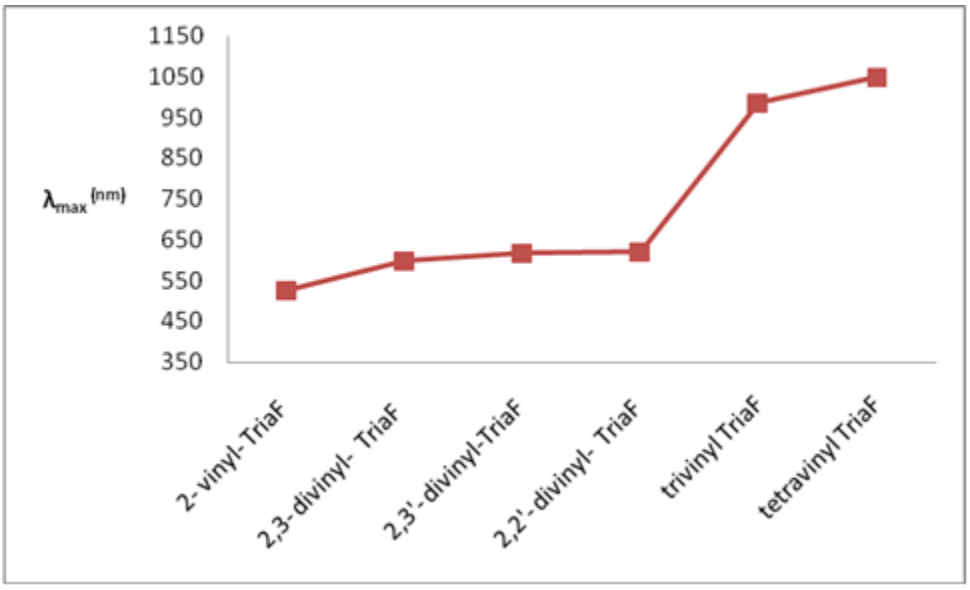


Figure 2. Different vinyl substituents and λmax (TD-DFT PBEPBE/6-311++G(2d,p)

3.1 UV- Visible Spectral studies on various substituent of Triafulvalene

Density functional calculations at PBEPBE using 6-311++G(2d,p) methods have been used to determine the structures of triafulvene and analogues. UV-Visible excitation properties are determined using excited state calculations using Time Dependent Density Fuctional Theory using the PBEPBE functional (TD-DFT PBEPBE) method using 6-311++G(2d,p) basis set. The various singlet electronic transitions to the first 50 excited states are studied. There will be numerous theoretically possible transitions, but the prominent transition with appreciable intensity/oscillator strength is only discussed here.

A UV-Visible spectrum is usually obtained as a result of electronic excitation from HOMO to LUMO's. As there are many possible LUMO's like LUMO (0), LUMO (+1), LUMO (+2) etc, multiple excitation peaks are possible in the spectra, but of varying intensities. As the HOMO-LUMO (n) gap increases, energy needed for excitation increases, hence λ decreases. More the conjugation more will be λ.

To study the effect of functional groups on λ_{max} of triafulvalene, hydrogen was replaced by various substituent like –CH=CH_2, -CHO, -OH, -CN, -NH_2, -NO_2 and -Cl. The molecules used are triafulvalene (A), mono substituted fulvalenes (B) and di substituted fulvalenes (C, D and E), where Y= –CH=CH_2, -CHO, -OH, -CN, -NH_2, -NO_2 and -Cl.

The λ_{max} various mono substituent are tabulated below. The data shows that +M groups like vinyl, -OH, -NH_2, and –Cl causes a decrease in λ_{max} value, while –M groups causes an increase in λ_{max} value. Fulvalene is unstable due to lack of aromaticity, the following trend occur maybe because, the -M groups decreases the electron density by electron withdrawal, whereas the +M group increases electron density in the ring by electron donation.

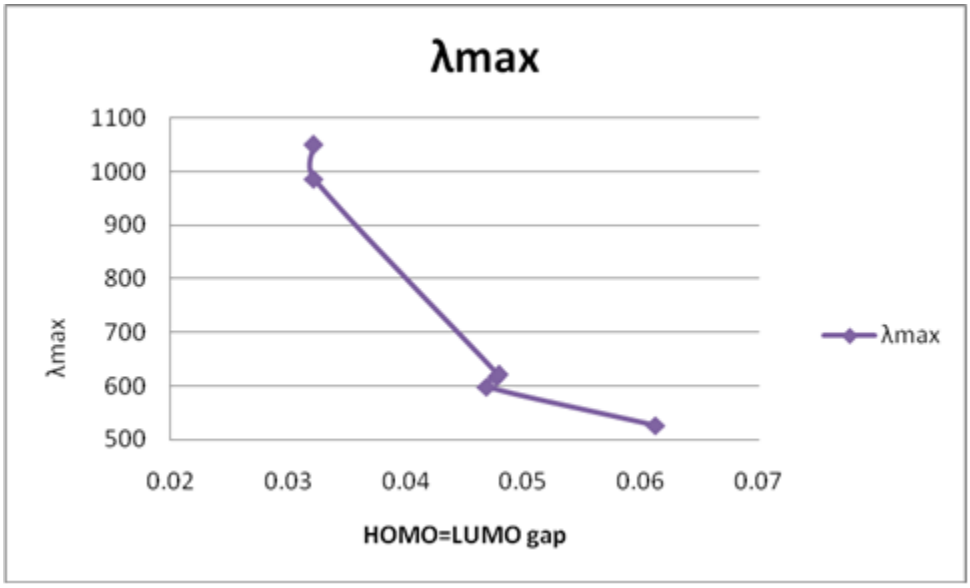


Figure 3. Energy gap (PBEPBE/6-311++G(2d,p)) and λmax (TD-DFT PBEPBE/6-311++G(2d,p) of various vinyl substituted TriaF

The λ_{max} of different substituted traifulvalenes are given in the table S1 (please see supplementary information). It indicates that the highest value of λ_{max} is for the nitro substituted triafulvalene followed by aldehyde, cyano, vinyl, unsubstituted, alcohol, chloro and amino derivatives. The substituents with multiple bond (vinyl, cyano, aldehyde, nitro) tends to show more λ_{max} than the others (amino, hydroxyl, chloro) even though the later groups are +M, capable of donating their lone pair to the triafulvalene ring. It is found from the optimized geometries that the former set of substituents with multiple bond participate in the conjugation of the triafulvalene backbone, enabling faster electronic transitions.

3.2 Electronic spectra of vinyl and cyano substituted triafulvalenes

An attempt is made to study the effect of number of substituents ion the UV spectra of the triafulvalene derivatives. The present study reports the effect of vinyl and cyano substituents. It is invariably found that as the number of the groups increase, λmax increases due to increased conjugation in the triafulvalene (TriaF) back bone. The HOMO- LUMO gap is different for the different disubstituted derivatives. It is found that the λmax is inversely proportional to the energy gap; as more the energy gap, more energy is required for the electronic transition.

The λ_{max} of various vinyl substituent are presented in table S2 (please see supplementary information). The figure 2 shows the variation of λmax with increase in the number vinyl substituent. It is evident that the λmax increases with an increase in conjugation from various vinyl groups. Figure 3 shows how the λmax is varied with the HOMO-LUMO gap, which indicates a general inverse relationship.

Table 1. Energy gap (PBEPBE/6-311++G(2d,p)), λmax (TD-DFT PBEPBE/6-311++G(2d,p) and extend of cyano substitution.

Compounds	HOMO	LUMO	LUMO-HOMO	λmax	f
2-cyano TriaF	-0.16911	-0.10594	0.06317	554.82	0.0599
2,3-dicyano TriaF	-0.19047	-0.15219	0.03828	889.99	0.0177
2,2'-dicyano TriaF	-0.19405	-0.12802	0.06603	534.62	0.0761
2,3'-dicyano fulvalene	-0.19522	-0.13255	0.06267	557.43	0.1204
tricyanoTriaF	-0.21356	-0.16901	0.04455	794.62	0.02
tetracyano TriaF	-0.2312	-0.18124	0.04996	723.84	0.0393

3.3 Electronic spectra of cyano substituted triafulvalenes

The table 1 represents the trend in λmax of different cyano substituted triafulvalenes. Figure 4 represents the variation of with the HOMO-LUMO energy gap and it is quite evident that the λmax increases with a decrease in the energy gap.

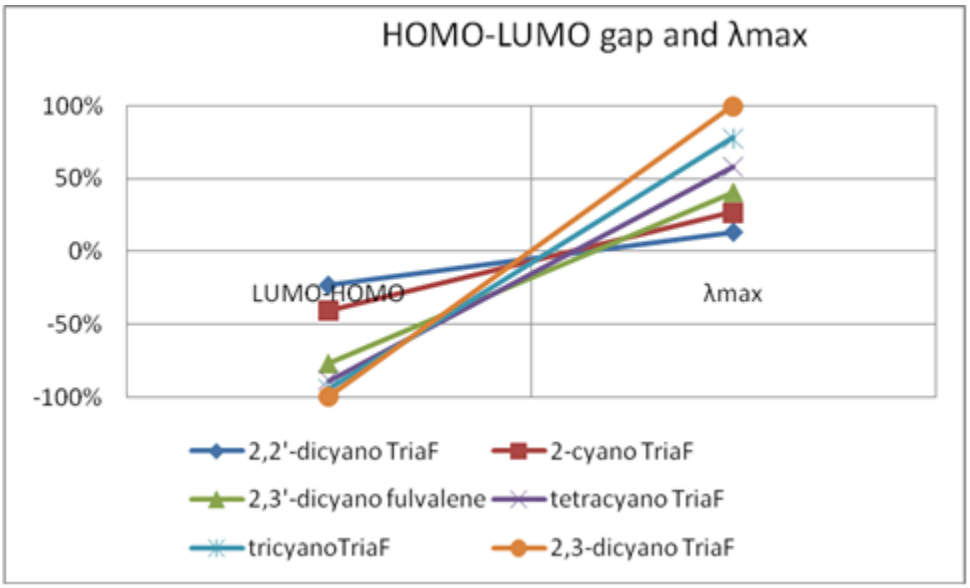


Figure 4. Dependence of λmax (TD-DFT PBEPBE/6-311++G(2d,p))with HOMO-LUMO energy gap (PBEPBE/6-311++G(2d,p)) for different cyano substituted TriaF.

4. CONCLUSION

Fulvalenes are a class of organic molecule of immense theoretical interest. UV Spectra of this class compound is difficult to take experimentally due to the instability of the compound. Theoretical chemistry methods are very useful in such scenario. The effects of substituent's on the UV spectra of such compounds are studied in article and it is found that the presence of a substituent with multiple bond enhances the electronic transitions and as the number of such groups increases, the absorption maxima increases. These information may aid in the design of novel synthetic techniques for these class of compounds.

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The authors declare no conflict of interest

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