



## A Semiempirical Study of Novel Carbazole based Dendrimers

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### ABSTRACT

A new semiempirical model of computational quantum chemistry, Parametric Model 6 (PM6) has been applied to study the absorption energies of a series of newly synthesized carbazole based dendrimers that possess excellent optoelectronic properties. The molecular structures of the dendrimers in the ground electronic state and their absorption energies (in vacuum and dichloromethane) have been computed using the PM6 and CIS-PM6 models, respectively, as implemented in MOPAC2009 software. The molecular structures of the dendrimers in the ground electronic state and their absorption energies in vacuum were also computed using the AM1 and ZINDO models, respectively, as implemented in Gaussian03 software. The computed absorption energies were found to linearly correlate with the reported absorption energies of the novel dendrimers. The CIS-PM6 model was found to be as powerful as the most widely used ZINDO model in predicting the absorption energies of the dendrimers.

### Introduction

The development of fast computers has revolutionized the field of computational chemistry. Now days, the techniques of computational chemistry are increasingly being used by scientists and engineers to predict various properties of matter. All electronic structure methods are based on the approximate solutions of the Schrödinger equation ( $H\Psi=E\Psi$ ). Electronic structure methods are broadly categorized into three groups: ab initio, density functional theory (DFT), and semiempirical methods. Ab initio and density functional theory methods are generally more time consuming than semiempirical methods because of the partial inclusion of empirical data in semiempirical model equations which has the overall effect of

time. Excited state simulations require more time than ground state simulations. Presently, Ab initio and DFT methods for treating excited states are more or less restricted to small molecular systems because of the huge computational time required (Bartell *et al.*, 2010; Bakalova and Kaneti, 2000). On the other hand, semiempirical methods allow fast treatment of the excited states of very large systems (Bartell *et al.*, 2010). The reliability of computational results depends on their ability to reproduce or correlate with the experimental data.

Absorption energy is the difference between the energy of the ground electronic state ( $S_0$ ) and the energies of various excited electronic states at the equilibrium geometry of the ground electronic state.

The intensities of absorption bands in electronic (UV/VIS) spectra are directly proportional to oscillator strengths of the excited electronic states. Electronic

transition to the excited state with the highest oscillator strength is the one responsible for maximum absorption band, the so called  $\lambda_{\max}$  (Bakalova and Kaneti, 2000).

This paper focuses on the semiempirical modelling of the absorption energies of novel carbazole based dendrimers developed by Adhikari *et al.* (2009). A dendrimer is a large branched molecule that contains an inner core and arms that can hold a various substituents. Many derivatives of carbazole have been synthesized and organic electronic devices based on these derivatives were investigated (Adhikari *et al.*, 2007). Carbazole derivatives are widely used as the materials for fabricating hole-transporting layers of organic light emitting diodes (OLEDs), utilizing their high charge mobility and thermal stability. Carbazole derivatives are also well known for their intense luminescence and are widely used as blue, green, red, and white emitters (Lee *et al.*, 2002; Ding *et al.*, 2006; Liu *et al.*, 2006).

Most of the published semiempirical modelling of absorption energies is carried out using ZINDO/S (Zerner's intermediate neglect of differential overlap/spectroscopic) model contained in Gaussian suite of programs (Frisch *et al.*, 2004). However, the ZINDO model as implemented in Gaussian suite of programs does not permit evaluation of solvent effects on absorption energies. The solvent effects can be computed using other semiempirical models such as Austin Model 1 (AM1) or Parametric Model 3 (PM3) along with a configuration interaction (CI) calculation such as CI singles (CIS) to compute absorption energies in various solvents (Bakalova and Kaneti, 2009). This is often achieved with the use of MOPAC software (Dewar *et al.*, 1985, www.openmopac.net, 2011). Rece

(MOPAC2009) contains a new semiempirical Parametric Model 6 (PM6) which is the first major improvement in methodology to MOPAC software, since the introduction of PM3 in 1989 (www.openmopac.net, 2011). The reliability of the PM6 model has been established for many ground state properties such as heats of formation, geometries, hydrogen bonding, acidity, etc (Gonçalves *et al.*, 2010, www.openmopac.net, 2011). Herein, the PM6 model has been used to compute the absorption energies of four carbazole based dendrimers in vacuum and in dichloromethane. The results were compared with the experimental absorption energies reported by Adhikari *et al.* (2009), and the absorption energies computed using the ZINDO model.

## Methodology

Two-dimensional structures of the investigated dendrimers were drawn using the ACD/ChemSketch software (www.acdlabs.com, 2010). The two-dimensional structures were then converted to three-dimensional structures with the aid of ACD/3D Viewer software (www.acdlabs.com, 2010). The three dimensional geometries were then used to prepare Gaussian input files for the computation of the equilibrium molecular structures of the dendrimers in the ground electronic state ( $S_0$ ) using the AM1 model (Frisch *et al.*, 2004). The equilibrium  $S_0$  geometries were then used for computing absorption energies using the ZINDO model as implemented in Gaussian 03 (Frisch *et al.*, 2004). MOPAC input files were then prepared for the computation of the equilibrium  $S_0$  molecular structures of the dendrimers and their absorption energies using the PM6 and the CIS-PM6 models, respectively, as implemented in

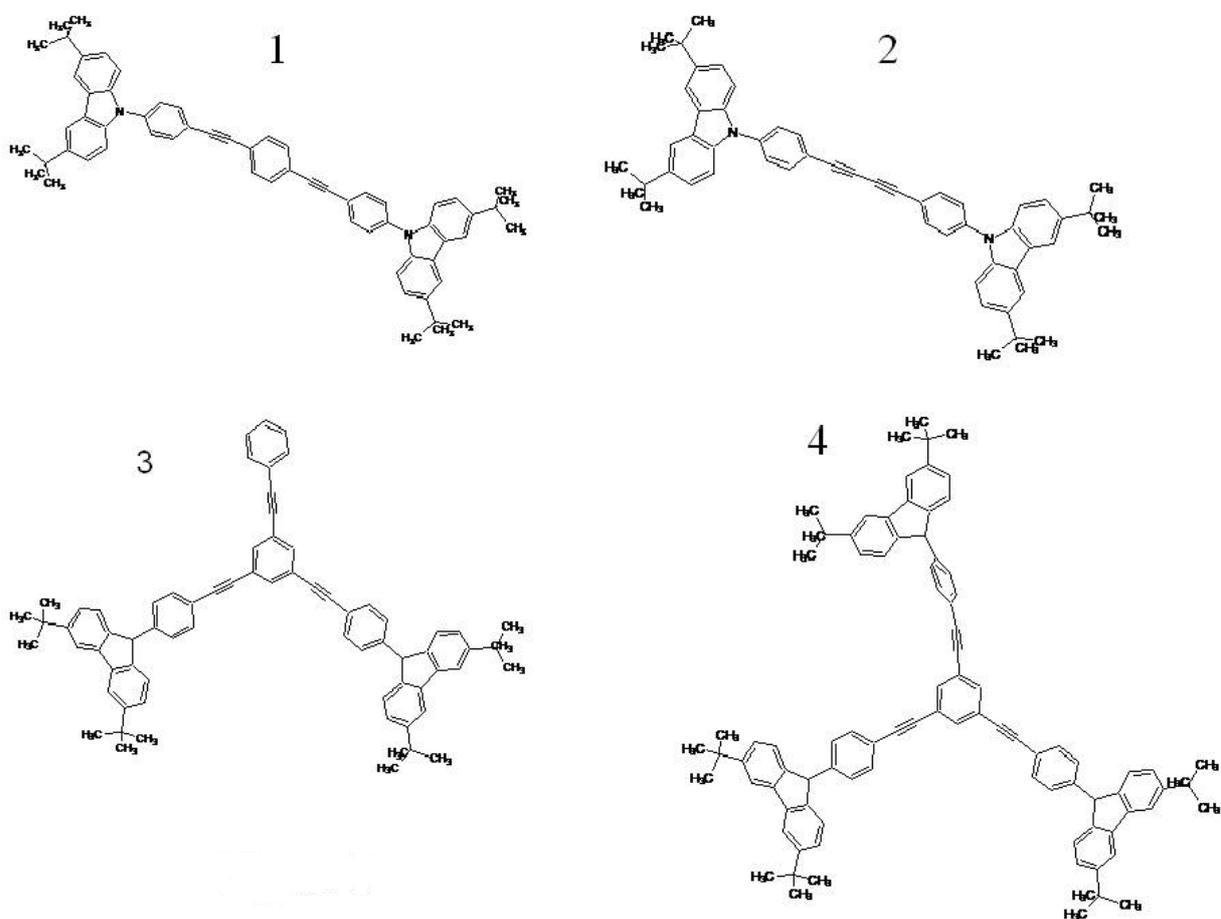
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The effect of dichloromethane solvent on the equilibrium  $S_0$  geometries and

absorption energies was accounted for by the Conductor-like Screening Model

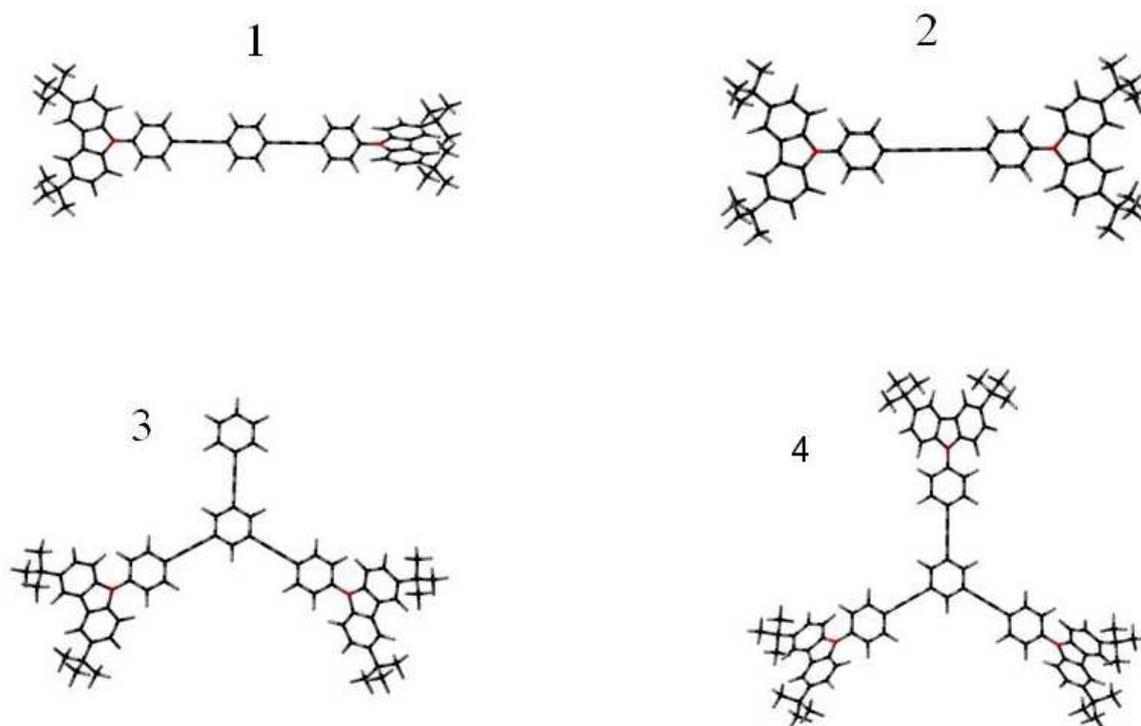
(COSMO) using the dielectric constant of 9.08 for dichloromethane. The following MOPAC keywords were used when computing absorption energies using the CIS-PM6, model: PM6, PRECISE, CIS, MECI, C.I.=10, and EPS=9.08 (for solvent effect).

The two-dimensional structures of the investigated dendrimers (1-4) are displayed in Figure 1. The optimized three-dimensional ground state structures of the four dendrimers shown in Figure 2 are non planar. The phenylethynyl cores of the dendrimers are planar; hence, the phenyl and ethynyl parts of the cores are fully conjugated. Whereas the carbazole arms are rotated from the plane of the phenylethynyl cores by 43 - 44°. The presence of the carbazole arms has led to the nonplanarity of the dendrimers.

## Results and Discussion



**Figure 1** Two-dimensional structures of the studied dendrimers



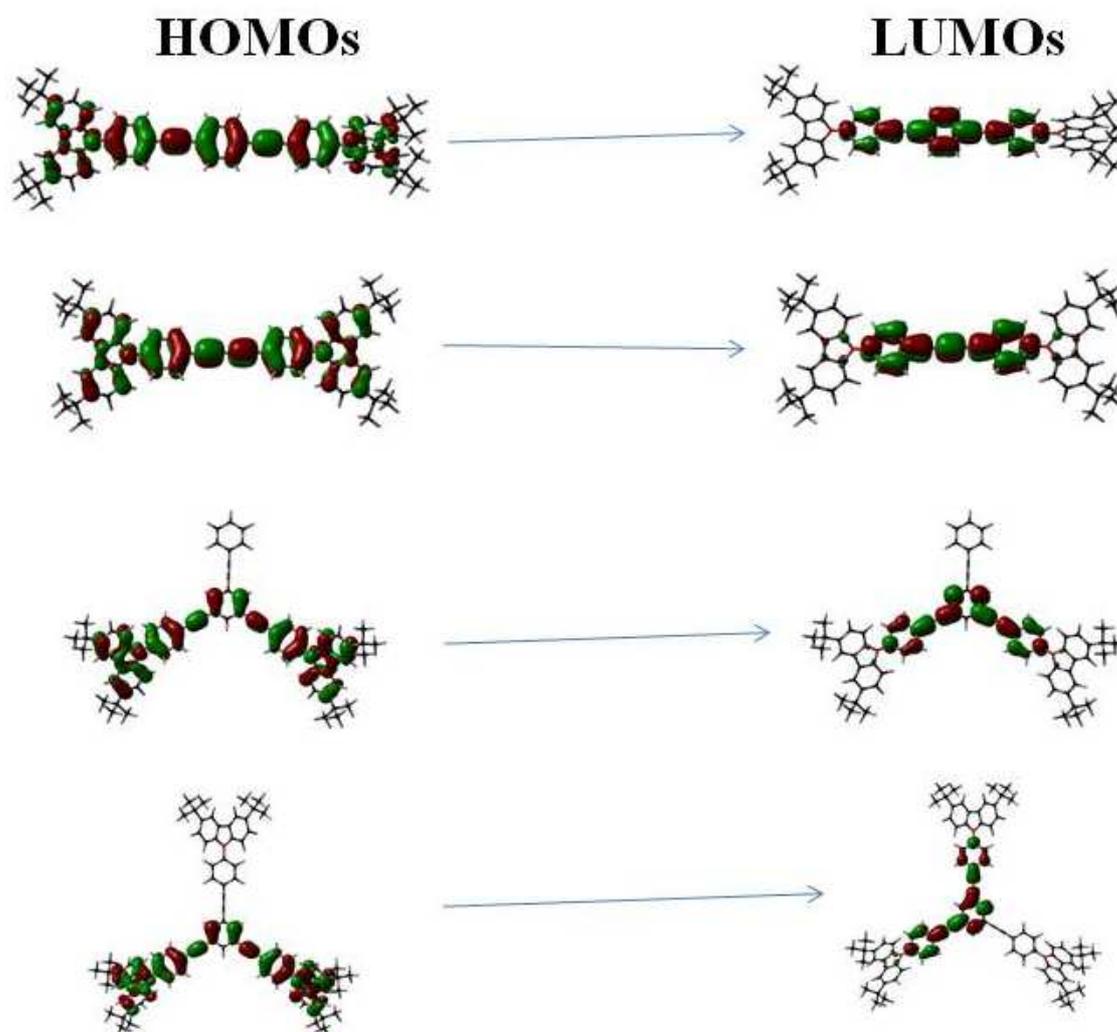
**Figure 2:** Optimized ground state geometries of the studied dendrimers

The calculated vertical excitation (absorption) energies and oscillator strengths of the first ten excited singlet states of each dendrimer are listed in Table 1. For all the dendrimers, excitation to the first excited state has the highest oscillator strength. The  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  transitions of dendrimer 4 are degenerate (have the same energy and oscillator strengths) which can be attributed to the  $C_3$  symmetry of dendrimer 4. Therefore, the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  transitions of dendrimer 4 can be treated as its first transition ( $S_0 \rightarrow S_1$  transition). Therefore, the maximum absorption band of each of dendrimer is due to electronic transition from the ground electronic state to the first excited singlet state ( $S_0 \rightarrow S_1$  transition). The results of the calculations also show that the  $S_0 \rightarrow S_1$  transitions of the

dendrimers are mainly assigned to electronic transition from the highest occupied molecular orbitals (HOMOs) to the lowest unoccupied molecular orbitals (LUMOs). As shown in Figure 3, the HOMOs of the dendrimers spread over the carbazole arms and the central phenylethynyl moiety; while the LUMOs are localized on the central phenylethynyl moiety. This shows that some of the electron density on the carbazole arms transfers to the central phenylethynyl moiety upon  $S_0 \rightarrow S_1$  transition of the dendrimers. Therefore, the  $S_1$  states of the dendrimers possess some charge-transfer character, the consequence of which is the strong dependence of their emission spectra on solvent polarity (Bakalova and Kaneti, 2000).

**Table 1:** ZINDO calculated absorption energies ( $A, \text{cm}^{-1}$ ) of the first ten excited singlet states of the studied dendrimers and their corresponding oscillator strengths ( $f$ )

Excited state	Dendrimer							
	1		2		3		4	
	$A, \text{cm}^{-1}$	$f$						
1	26330	2.166	25558	0.912	28570	1.678	28236	1.744
2	29343	0.000	26666	0.001	29181	0.846	28236	1.744
3	29390	0.000	28817	0.000	30521	0.401	29221	0.000
4	29719	0.000	29612	0.000	30598	0.000	29472	0.003
5	29751	0.046	29659	0.242	30974	0.004	29472	0.003
6	30631	0.000	32135	0.000	30994	0.003	29948	0.026
7	32131	0.073	32144	0.182	32689	0.026	29948	0.026
8	32133	0.115	32317	0.000	32700	0.238	30042	0.000
9	32910	0.002	32828	0.000	33206	0.021	30514	0.000
10	32914	0.050	32840	0.059	33217	0.065	31431	0.053



**Figure 3** Calculated electron density surfaces for the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the studied dendrimers

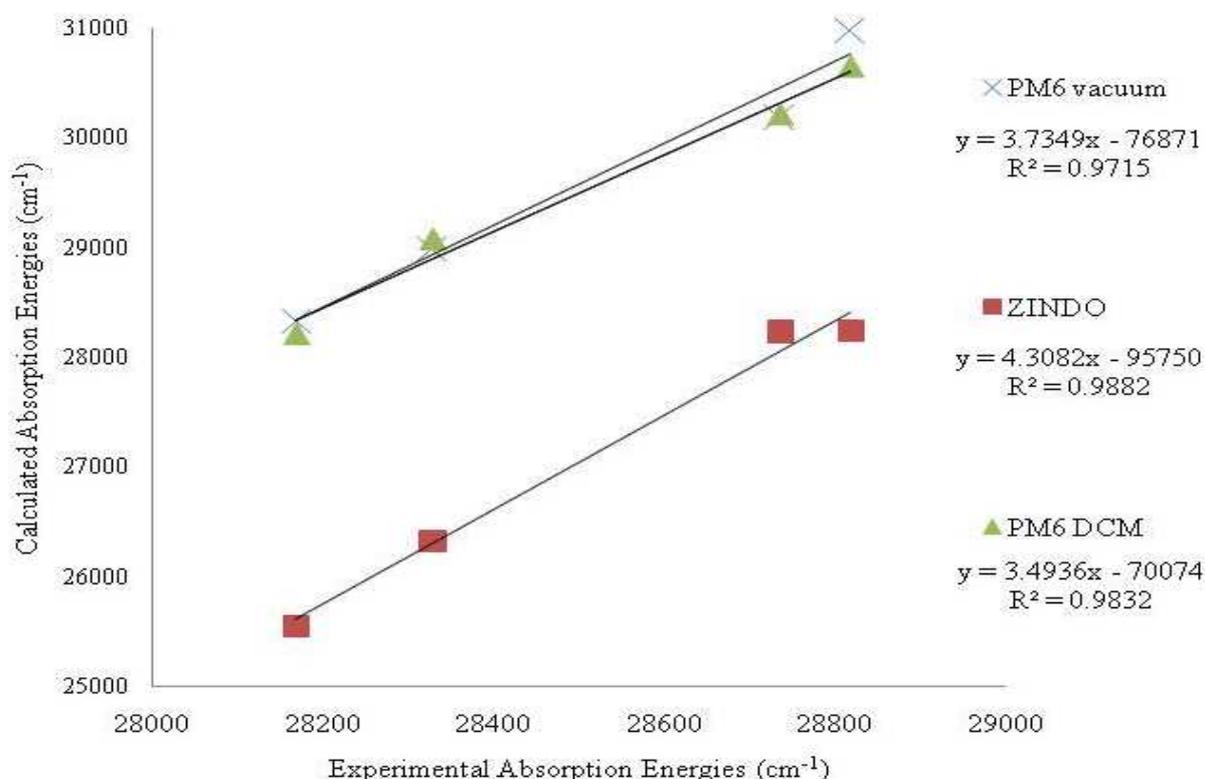
Table 2 presents the experimental and calculated absorption energies of the dendrimers using ZINDO model in vacuum, as well as using the CIS-PM6 model in vacuum and in dichloromethane (DCM). The experimental absorption spectra of the dendrimers were recorded in dichloromethane (Adhikari *et al.*, 2009). Figure 4 shows that a linear relationship exists between the experimental and calculated absorption energies of the dendrimers for both ZINDO and CIS-PM6 models. Also shown in Figure 4 are the model equations that express the calculated absorption energies as a function of the experimental absorption

energies, and their corresponding  $R^2$  values. A slightly better correlation is found for the ZINDO model and the CIS-PM6 result that includes the effect of dichloromethane (DCM) solvent. However, the mean deviation of the absorption energies predicted by the CIS-PM6 model in dichloromethane from the experimental absorption energies is  $1025\text{ cm}^{-1}$ . For the ZINDO model, the mean deviation is  $1424\text{ cm}^{-1}$ . The CIS-PM6 absorption energies in vacuum and in dichloromethane have similar values (differ by an average of  $82\text{ cm}^{-1}$ ) due to the low polarity of dichloromethane.

**Table 2.** Experimental and calculated absorption energies ( $A_{\text{max}}$ ,  $\text{cm}^{-1}$ ) by ZINDO, and CIS-PM6 models in vacuum and dichloromethane

Dendrimer	Experimental (Dichloromethane) <sup>a</sup>	CIS-PM6 (Dichloromethane)	CIS-PM6 (Vacuum)	ZINDO (Vacuum)
1	28329	29077	28990	26330
2	28169	28212	28327	25558
3	28736	30213	30187	28570
4	28818	30650	30979	28236

<sup>a</sup>Taken from Adhikari *et al.*, (2009)



**Figure 4** Relationship between experimental and calculated absorption energies (in  $\text{cm}^{-1}$ ) of the studied dendrimers

## Conclusion

The studied dendrimers are non planar due to the rotation of the carbazole arms from the central phenylethynyl core by 43-44°. The maximum absorption bands of the four dendrimers are due to electronic transition from the ground electronic state to the first excited singlet state ( $S_0 \rightarrow S_1$  transition). Analysis of the HOMOs and

LUMOs of the dendrimers suggest that the  $S_1$  states of the dendrimers possess some charge-transfer character. The computed absorption energies of the dendrimers linearly correlate with the experimental absorption energies. The CIS-PM6 model is found to be as powerful as the most widely used ZINDO model in predicting the absorption energies of dendrimers.

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