

Full Length Research Paper

Chemistry of benzobispyrrole-derived squaraines

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In the search for a conducting polymers with narrow Energy Band-Gap (E_g), the research focus is centered on increasing the bandwidth of the Highest Occupied Molecular Orbitals (HOMO) or the Lowest Orbital Molecular Orbitals (LUMO) of a conducting polymers through the use of strong electron donor or strong electron acceptor, respectively. In this research, we considered the trend of change in E_g , UV absorption, IR absorption, Density of State (DOS) and Excited state Properties of various forms of Benzobispyrrole-Derived Squaraines using Density Functional Theory (DFT) and Hartree-Fock (HF) methods. The results obtained from various computational methods employed are in good agreement with literature, which observed that the E_g values calculated with ROHF is higher than the expected value, while that calculated with BLYP and SVWN values are about 40 to 50% lower than the expected. The better E_g values in good agreement with expected values are found by hybrid functional B3LYP. However, there is a good correlation in the trend of change in the calculated E_g values of all computational methods with the trend of change in the experimental E_g . Also, DOS, IR Maximum Absorption, Dipole Moment and UV Absorption add meaning to the intrinsic conductivities property of the models.

Key words: Highest occupied molecular orbitals (HOMO), lowest orbital molecular orbitals (LUMO), band gap, UV absorption, density functional theory (DFT), Hartree-Fock (HF) methods, density of state (DOS).

INTRODUCTION

There is a high interest in π -conjugated polymers due to their numerous remarkable characteristics (Frommer and Chance, 1986) such as intrinsic semiconducting properties (Roncali, 1997), non-linear optical behaviour, and exceptional mechanical properties (Roberts and Jenekhe, 1994) such as tensile strength and resistance to harsh environments. These properties is traceable to extensive delocalization of π -electrons.

The advantages of the conducting polymers are shown in terms of their processibility and plastics nature, which make them to combine the mechanical properties such as flexibility, toughness, malleability, elasticity, etc; with high intrinsic conductivities. These properties can be improved through various methods of organic synthesis (Naarmann, 2002). Mostly, the polymers that are of outstanding application for these applications are those that contain aromatic and heteroaromatic ring structures (Neuse, 1982).

In this study, we considered squaraines dyes, which is a significant type of π -conjugated polymers that belongs to the class of polymethyne dyes with highly colored, resonance-stabilized zwitterionic structures with an intense absorption in the visible to the near-infrared region (Ajayaghosh, 2005). Squaraines are generally prepared by the condensation of electron-rich aromatic or heterocyclic compounds, such as N,N-dialkylanilines, benzothiazoles, phenols, azulenes, and pyrroles with 3,4-dihydroxy-3-cyclobutene-1,2-dione (squaric acid) (Maahs and Hegenberg, 1966; Sprenger and Ziegenbein, 1966).

The synthesis is through the reaction of electron rich aromatic compounds with electron deficient squaric acid, which will result in the formation of polymeric dyes with extended conjugation. The possibility of synthesizing a variety of electron-rich aromatic and heterocyclic systems, which can react with squaric acid, has increased the design of variety of symmetrical and unsymmetrical squaraines with tunable optical properties (Ajayaghosh, 2005).

In order to obtain a conjugated polymers with high intrinsic conductivity, there is need to make use of an

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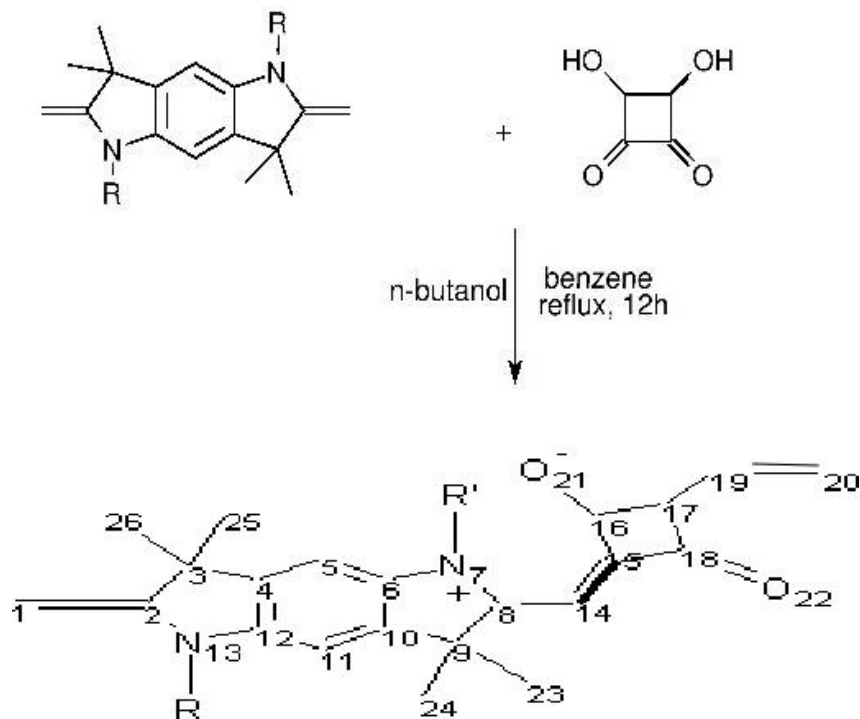


Figure 1. Benzobispyrrole derived polysquaraines (BP) structure showing the common parts of the geometries of BP1, BP2, BP3, BP4 and BP5 (Ajayaghosh, 2003a).

Table 1. Names of benzobispyrrole derived polysquaraines.

No.	Definition	Name
I	R=H	BP1
II	R=CH ₃	BP2
III	R=C ₄ H ₉	BP3
IV	R=C ₇ H ₁₅	BP4
V	R=C ₁₂ H ₂₅	BP5

organic dyes with inherently low HOMO-LUMO energy gap as building blocks. Squaraines is one of the rare π -conjugated polymers that have high intrinsic conductivity, which are characterized with near-IR wavelength absorption (Arunkumar et al., 2006), (Thomas et al., 1997) and low E_g (Cho et al., 2002), (Tsuda and Osuka, 2001). The low E_g value, favorable optical properties, photostable and immense flexibility for synthetic manipulation (Lu et al., 2004) make squaraines to have a wide application in photonic devices (Ajayaghosh, 2003a) like organic solar cells (Law, 1988), photodynamic therapeutics (Arunkumar et al., 2006; Jyothish, 2007), chemosensor, xerographic sensitizers, optical recording media (Emmelius et al., 1989) and photoreceptors (Tam, 1980).

The modeled squaraines dyes considered in this

research are the products of the condensation of benzobispyrrole with squaric acid (Ajayaghosh, 2003a, b). The products are given trivial name "BP".

The names of benzobispyrrole derived polysquaraines (Figure 1) are given in Table 1.

COMPUTATIONAL DETAILS

Gaussian 03 package (Frisch et al., 2003) was used for all the calculations, and all the computation were done at Temperature of 298.15K and a pressure of 1 atm.

The geometries of BP1, BP2, BP3, BP4 and BP5 were fully optimized at Hartree-Fock (ROHF) level, Density Functional Theory (DFT) level with the local functionals (SVWN, BLYP) and Hybrid Functional B3LYP (Parr and Yang, 1989; Bartolotti and Fluchick, 1996) with the 6-311G basis sets (Frisch et al., 1984). The purpose of using many functionals is to discover which one will best

Table 2. The Mulliken atomic charges of BP1, BP2, BP3, BP4 and BP5.

Definition	BP1	BP2	BP3	BP4	BP5
C ₁	-0.37	-0.37	-0.36	-0.36	-0.36
C ₂	0.6	0.46	0.46	0.46	0.46
C ₃	0.39	-0.37	-0.38	-0.38	-0.38
C ₄	-0.09	-0.1	-0.1	-0.09	-0.09
C ₅	0.02	0.02	0.03	0.02	0.02
C ₆	0.32	0.31	0.21	0.29	0.29
N ₇	-0.84	-0.76	-0.77	-0.75	-0.75
C ₈	0.45	0.46	0.49	0.5	0.5
C ₉	-0.43	-0.43	-0.44	-0.46	-0.46
C ₁₀	-0.06	-0.05	-0.04	-0.02	-0.02
C ₁₁	-0.01	0	0	0	0
C ₁₂	0.37	0.37	0.36	0.37	0.37
N ₁₃	-0.89	-0.81	-0.81	-0.82	-0.82
C ₁₄	0.01	-0.1	-0.11	-0.09	-0.09
C ₁₅	-0.15	-0.07	-0.08	-0.08	-0.08
C ₁₆	0.15	0.18	0.19	0.18	0.18
C ₁₇	-0.09	0.09	-0.07	-0.06	-0.06
C ₁₈	0.15	0.12	0.1	0.1	0.1
C ₁₉	-0.01	-0.02	-0.01	-0.01	-0.01
C ₂₀	-0.32	-0.32	-0.31	-0.31	-0.32
O ₂₁	-0.49	-0.43	-0.43	-0.44	-0.44
O ₂₂	-0.38	-0.4	-0.4	-0.4	-0.4
C ₂₃	-0.45	-0.45	-0.46	-0.45	-0.46
C ₂₄	-0.45	-0.45	-0.45	-0.46	-0.45
C ₂₅	-0.45	-0.45	-0.45	-0.45	-0.45
C ₂₆	-0.45	-0.45	-0.45	-0.45	-0.45

explain the trend of change in the experimentally available E_g values and also give a relatively close values.

The molecular energy gap (E_g), between ground and excited states was calculated as the LUMO- HOMO energy difference:

$$E_g = E_{\text{HOMO}}^i - E_{\text{LUMO}}^i$$

where E_{HOMO}^i is the highest orbital energy of HOMO, and E_{LUMO}^i is the lowest orbital energy of LUMO.

Also the excited state properties were calculated with the aid of the configuration interaction singlet (CIS) approach and a basis set of 6-311+G. One diffusion function is included in the basis set in order to improve the accuracy of the excited state properties as it was reported by Foresman and Frisch (1996) that it gives a better result for excited state properties calculation by CIS functional.

We computed the properties of 5 excited state with the keyword Nstates = 5. For the larger models with a basis set more than 200, an equation that uses AO integrals and recomputed them as they are needed was used through the keyword CIS = Direct.

We built the Monomers as Donor-Acceptor (D-A) and D-A-D-A as Dimers using Gabedit package (Allouche, 2007). The monomers were allowed to bond to extra carbon outside the normal unit to represent the continuity of the structure. Also all the gaussian input files were prepared using Gabedit.

The purpose of considering the monomers and the dimers is to see if just D-A of the monomers will give a E_g and UV values that are close and good enough to explain the trend of change in the

experimental E_g values in order to reduce the computational cost of using D-A-D or D-A-D-A. More so to see if the same trend of change can be reproduced when considering the dimers.

The DOS values were extracted with the help of Gausssum package (Boyle, 2007) from the Gaussian log file, where population analysis of optimized geometry has been calculated. And the plots were done with the help of gnuplot.

RESULTS AND DISCUSSION

Geometry

Table 2 shows the effect of alkylation on the Mulliken Atomic Charges. There is a decrease in the Mulliken Atomic Negative Charges on the Nitrogen atoms of the Pyrrole units and an increase in Mulliken Atomic Negative Charges on the Oxygen atoms on the Squaric unit. This could be responsible for the increase in N_7-C_8 bond length and the decrease in $C_{16}-O_{21}$ bond length (Table 3).

The effect of more electrons being pulled toward the squaric unit due to alkylation can be seen on the Carbon Atoms on both sides of N_7 . There is an increase in Negative Charge on C_8 that is close to Squaric unit and decrease in Negative Charge on C_6 .

Table 3. Various bond lengths of the main structure of BP1, BP2, BP3, BP4 and BP5 from Figure 1.

Definition	BP1	BP2	BP3	BP4	BP5
C ₁ =C ₂	1.34	1.34	1.34	1.34	1.34
C ₂ -C ₃	1.55	1.55	1.55	1.55	1.55
C ₂ -N ₁₃	1.41	1.41	1.41	1.41	1.41
C ₃ -C ₄	1.53	1.53	1.53	1.53	1.53
C ₃ -C ₂₅	1.55	1.55	1.55	1.55	1.55
C ₃ -C ₂₆	1.55	1.55	1.55	1.55	1.55
C ₄ -C ₅	1.39	1.39	1.39	1.39	1.39
C ₄ =C ₁₂	1.41	1.41	1.41	1.41	1.41
C ₅ =C ₆	1.4	1.4	1.4	1.4	1.4
C ₆ -N ₇	1.41	1.43	1.43	1.43	1.43
C ₆ -C ₁₀	1.4	1.4	1.4	1.4	1.4
N ₇ -C ₈	1.34	1.35	1.35	1.35	1.35
C ₈ -C ₉	1.54	1.54	1.55	1.55	1.55
C ₉ -C ₁₀	1.53	1.52	1.52	1.52	1.52
C ₉ -C ₂₃	1.55	1.55	1.55	1.55	1.55
C ₉ -C ₂₄	1.55	1.55	1.55	1.55	1.55
C ₁₀ =C ₁₁	1.39	1.39	1.39	1.39	1.39
C ₁₁ -C ₁₂	1.4	1.4	1.4	1.4	1.4
C ₁₂ -N ₁₃	1.39	1.4	1.4	1.4	1.4
C ₈ -C ₁₄	1.41	1.4	1.41	1.41	1.41
C ₁₄ =C ₁₅	1.37	1.38	1.38	1.38	1.38
C ₁₅ -C ₁₆	1.49	1.51	1.51	1.51	1.51
C ₁₆ -C ₁₇	1.45	1.46	1.46	1.45	1.45
C ₁₆ -O ₂₁	1.27	1.26	1.26	1.26	1.26
C ₁₇ -C ₁₈	1.47	1.46	1.46	1.46	1.46
C ₁₈ =O ₂₂	1.25	1.25	1.25	1.25	1.25
C ₁₈ -C ₁₅	1.5	1.5	1.5	1.5	1.5
C ₁₇ -C ₁₉	1.42	1.42	1.42	1.42	1.42
C ₁₉ -C ₂₀	1.35	1.35	1.35	1.35	1.35

The multiple regression analysis was also carried out in order to know the significant and the correlation of change in the distribution of charges on C₆, C₈, N₇, O₂₁ and O₂₂ with the Eg values in all model Squaraines. The regression equation that relates the independent variables with Eg is:

$$E_g = 70.82 - 23.63 \cdot C_6 - 53.41 \cdot C_8 + 78.04 \cdot N_7 - 87.36 \cdot O_{21} + 37.17 \cdot O_{22}$$

From this equation, if the charges on the variables were equaled to zero, the Eg would have been very large as 70.82. Also from the equation, it can be seen that the change in the charge distribution on O₂₁ is the most significant, followed by N₇.

The $r^2 = 0.99$, which shows that 100% of the value of Eg is directly correlated with change in the distribution of the charges. Standard Error of the Estimation is 1.09E-13. The Average of the computational value of Eg is 2.31 and Average of Estimated Eg by regression is 2.31± 1.09E-13, which is approximately the same.

Table 4 shows the bonding distances and bonding angles of ground state structure of BP1 obtained by ROHF, BLYP, SWVN and B3LYP. The four Functionals give a relatively the same values.

Electronic and thermodynamic properties

The Eg values (Table 5) calculated on the monomers are larger than the experimental Eg values and this is understood since the monomers are D-A units and at least D-A-D unit is required to obtain a lower Eg that is close to experimental Eg. But the trend of change in their calculated Eg of this monomers gives an insight into change in the intrinsic conductivities of the models. Dimmers, which are D-A-D-A give better results.

There is increase in the bandwidth of HOMO and LUMO through polymerization, which is the result of increase in molecular orbitals. In monomers there is only one type of spectral, but there is contribution of alpha and beta spectral for the dimers.

Table 4. The bond distance in Å and bond angle in degree of optimized geometry of BP1.

Definition	B3LYP	BLYP	SVWN	ROHF
C ₁₇ -C ₁₉	1.42	1.43	1.41	1.44
C ₁₆ -C ₁₇	1.45	1.46	1.44	1.41
C ₁₇ -C ₁₈	1.47	1.49	1.47	1.44
C ₁₈ =O ₂₂	1.24	1.26	1.24	1.22
C ₁₆ -O ₂₁	1.27	1.29	1.27	1.25
C ₁₅ -C ₁₈	1.5	1.52	1.49	1.49
C ₁₄ =C ₁₅	1.37	1.39	1.37	1.35
C ₈ -C ₁₄	1.41	1.42	1.4	1.42
C ₈ =N ₉	1.34	1.36	1.34	1.31
C ₆ -C ₇	1.53	1.54	1.51	1.52
C ₅ =C ₆	1.39	1.4	1.38	1.39
C ₁₀ =C ₁₁	1.4	1.41	1.39	1.38
C ₄ -C ₅	1.4	1.41	1.4	1.39
C ₄ =C ₁₂	1.41	1.42	1.41	1.4
N ₂ -C ₃	1.41	1.42	1.39	1.4
C ₁₈ -C ₁₇ -C ₁₉	134.36	134.7	132.49	134.25
C ₁₇ -C ₁₆ -O ₂₁	136.84	136.41	136.56	138.24
C ₁₇ -C ₁₈ =O ₂₂	136.68	136.48	135.73	138.02
C ₁₇ -C ₁₈ -C ₁₅	89.18	89.16	89.41	89.08
C ₁₆ -C ₁₅ -C ₁₈	88.66	88.85	88.52	87.81
C ₈ =C ₁₄ -C ₁₅	123.89	124.28	122.86	123.6
C ₇ -C ₈ -C ₁₄	125.73	126.27	125.5	124.65
C ₇ -C ₈ =N ₉	109.07	108.86	109.43	109.52

The Eg calculated with ROHF correctly reproduced the trend of change due to alkylation on the experimental band-gap values, but the values are higher than the expected values because there is no correlation function in ROHF. From ROHF and B3LYP functionals, there is gradual decrease in calculated Eg from BP1 to BP3. But from BP4 to BP5 there is increase in Eg values, which can be explained to be the prominent effect of steric hindrance. The Eg values calculated by B3LYP functional are very closed to the experimental Eg values and thus shows that B3LYP functional gives better Eg values.

The values of Eg calculated by BLYP and SVWN are about 40 to 50% lower than experimental values. This is understood since DFT band plot is a representation of the DFT Kohn-Sham energies. The reason is that the Kohn-Sham electronic structure in DFT is not quasiparticle electronic structure of a system, and there is no Koopman theorem holding for Kohn-Sham energies, as there is for Hartree-Fock energies, which can be truly considered as an approximation for quasiparticle energies that can give the correct band energies of the system.

More so, the change in the DOS is significant in explaining change in the Eg. Alkylation of the monomers and the dimers of BP1 to BP3 resulted to an increase in maximum DOS found at the HOMO side of the molecular orbitals, which is in line with the decreasing values of

calculated Eg values accordingly (Figure 2). But after BT3, there is decrease or no change in the DOS, which explains further the reason for increasing Eg due to steric hindrance. Polymerization of monomers to dimers of BP1, BP2, BP3, BP4 and BP5 resulted to increase DOS of each (Figure 3) and consequently decrease in their Eg.

There are two different significant points of IR absorption (Figure 4), the maximum absorption at approximately 1612 cm⁻¹, which can be assigned to C=O on the squaric unit and the small absorption at approximately 3135 cm⁻¹, which should be the vibration due to C-H. The value 1612 cm⁻¹ assigned to the vibration of C=O is close to the value according to Carlos et al. (2006) and Lu et al., (2004). More so, from the experimental work of Law et al. (1986), there is no absorption at 1700 cm⁻¹, but a strong absorption of about 1600 cm⁻¹ was assigned to bond stretching of C=O in the four membered ring of squaranes, which is in good agreement with our computational result. The vibration at approximately 3135 cm⁻¹, increased in intensity due to alkylation from BP1 to BP5. Maximum absorption shows a significant pattern to further explain the change in Eg due to alkylation (Figure 4). An increase in the maximum absorption is observed from BP1 to BP2, which is in line with the calculated and experimentally available Eg, which show a decrease in Eg from BP1 to BP2. And just as in the experimentally available Eg values, the effect of

Table 5. Energy band gap of various squaraines dyes considered.

Squaraines type	Functional/basis set	Computation band-gap (Ev)		Experimental band-gap (Ev)
		Monomer	Dimer	
BP1	B3LYP/ 6-311G	2.35	1.28	1.15
	BLYP/ 6-311G	1.26	0.47	
	SWVN/ 6-311G	1.33		
	ROHF/ 6-311G	7.47	2.73	
BP2	B3LYP/ 6-311G	2.31	1.26	1.1
	BLYP/ 6-311G	1.25	0.46	
	SWVN/ 6-311G	1.32		
	ROHF/ 6-311G	7.44		
BP3	B3LYP/ 6-311G	2.29	1.24	1.2
	BLYP/ 6-311G	1.24	0.44	
	SWVN/ 6-311G	1.29		
	ROHF/ 6-311G	7.32	2.63	
BP4	B3LYP/ 6-311G	2.30	1.24	1.2
	BLYP/ 6-311G	1.25	0.44	
	SWVN/ 6-311G	1.31		
	ROHF/ 6-311G	7.39	2.64	
BP5	B3LYP/ 6-311G	2.30	1.24	1.15
	BLYP/ 6-311G	1.25	0.44	
	SWVN/ 6-311G	1.31		
	ROHF/ 6-311G	7.39	2.65	

The Experimental energy band gap values are from supplementary work of Ajayaghosh (2003b).

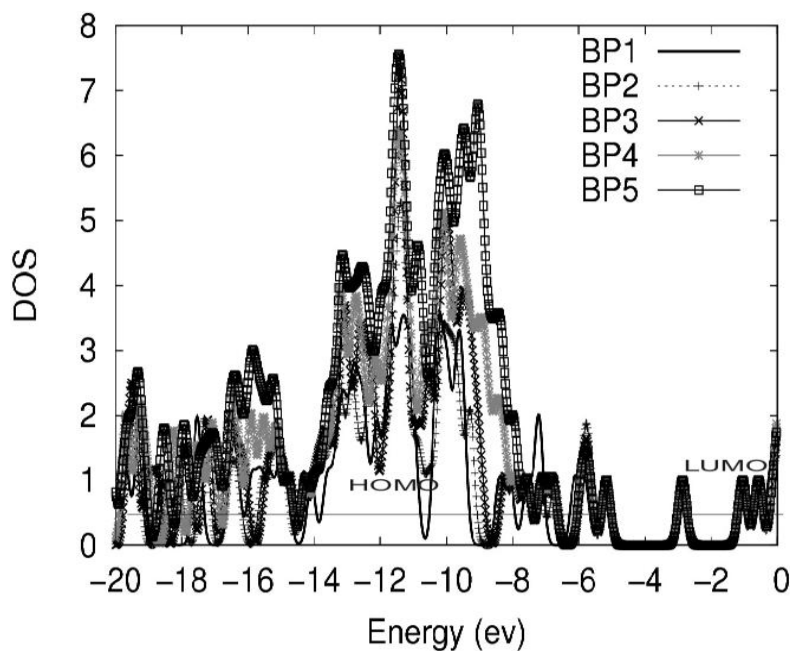


Figure 2. Energy band gap spectral showing the DOS of the monomers of BP1, BP2, BP3, BP4 and BP5 computed by B3LYP functional.

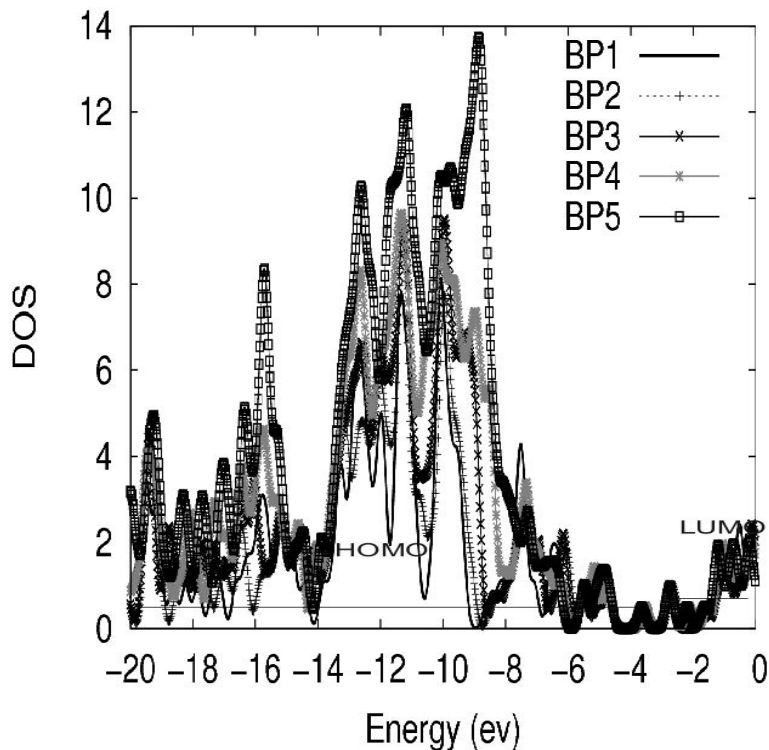


Figure 3. Energy band gap spectral showing the DOS of the Dimers of BP1, BP2, BP3, BP4 and BP5 computed by B3LYP functional (The DOS spectrum for the dimers is the average of Alpha DOS spectrum and Beta DOS spectrum).

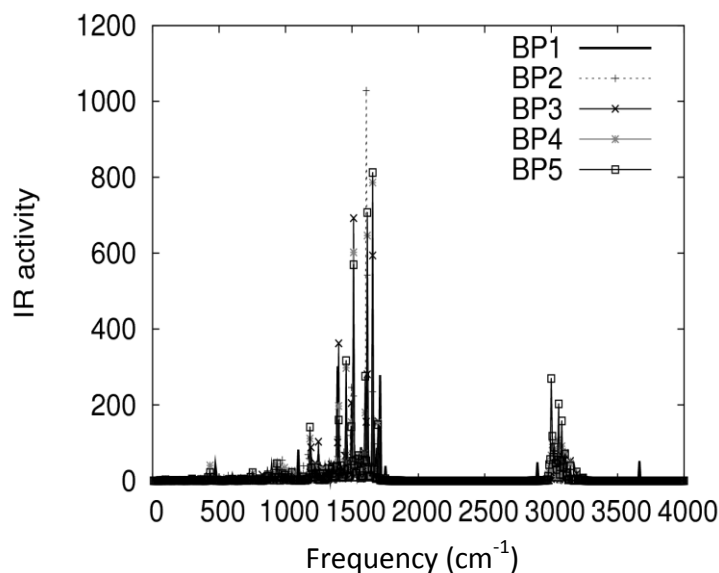


Figure 4. IR frequency Spectrals showing various absorption maximal of the Monomers of BP1 to BP5 computed by B3LYP functional.

steric hindrance that leads to increase in E_g values from BP3 to BP5 also followed with decrease in IR maximum absorption accordingly. More so, BP2, which has the lowest E_g from experimentally available values also has

the higher IR Maximum Absorption.

Table 6 shows that the Dipole Moment, which shows the direction on the x-axis plane regardless of the minus or plus sign, increase from BP1 to BP2, but decrease

Table 6. Thermodynamic properties of various squaraines dyes considered.

Squaraines type	Method used	Total energy (AU)	Dipole moment	Thermal (Kcal/Mol-K)	CV (Kcal/Mol-K)	S (Kcal/Mol-K)
BP1	B3LYP/6-311G	^D -2105.61 ^M -1111.44	^D 12.20 ^M -8.758	^D 474.90 ^M 260.11	^D 176.12 ^M 94.11	^D 265.28 ^M 164.06
	BLYP/6-311G	^D -2104.87 ^M -1111.04	^D 15.37 ^M -9.02	^D 461.37 ^M 252.79	^D 181.96 ^M 97.25	^D 270.76 ^M 166.97
	SVWN/6-311G	^M -1105.36	^M 8.90	^M 254.96	^M 95.35	^M 165.25
	ROHF/6-311G	^D -2092.01 ^M -1104.22	^D -9.62 ^M 9.48	^M 276.44	^M 87.96	^M 158.89
BP2	B3LYP/6-311G	^D -2262.77 ^M -1190.03	^D -13.35 ^M 10.26	^M 297.46	^M 105.33	^M 181.61
	BLYP/6-311G	^D -2261.93 ^M -1189.58	^D 16.55 ^M 10.36	^D 534.04 ^M 289.23	^D 205.82 ^M 108.78	^D 307.57 ^M 185.09
	SVWN/6-311G	^M -1183.52	^M 10.32	^M 291.63	^M 106.81	^M 182.25
	ROHF/6-311G	^M -1182.24	^M 12.00	^M 315.87	^M 98.38	^M 176.18
BP3	B3LYP/6-311G	^D -2734.53 ^M -1425.91	^D -13.31 ^M -10.19	^M 410.16	^M 133.99	^M 221.62
	BLYP/6-311G	^D -2733.38 ^M -1425.30	^D -16.75 ^M -10.38	^M 399.07	^M 138.33	^M 225.63
	SVWN/6-311G	^M -1418.11	^M -10.34	^M 401.71	^M 136	^M 222.24
	ROHF/6-311G	^M -1416.39	^M -11.45			
BP4	B3LYP/6-311G	^M -1661.78	^M -9.19	^M 522.71	^M 162.78	^M 266.71
	BLYP/6-311G	^D -3204.82 ^M -1661.02	^D -16.74 ^M -9.35	^M 508.75	^M 167.95	^M 270.59
	SVWN/6-311G	^M -1652.68	^M 9.63	^M 511.64	^M 165.32	^M 266.75
	ROHF/6-311G	^D -3184.62 ^M -1650.54	^D -12.22 ^M -10.25			
BP5	B3LYP/6-311G	^M -2054.90	^M 7.55	^M 710.39	^M 210.68	^M 337.85
	BLYP/6-311G	^D -3990.54 ^M -2053.89	^D -16.17 ^M 7.68	^M 691.65	^M 217.24	^M 342.96
	SVWN/6-311G	^M -2043.63	^M 8.20	^M 694.8	^M 214.14	^M 338.48
	ROHF/6-311G	^M -2040.79	^M 8.09			

CV stands for specific heat capacity, S stands for entropy and the superscripts M for monomer and D for dimer.

Table 7. Excited state properties of various monomers of squaraines dyes considered using functional/basis set of CIS/6-311+G.

	Excited state	Transition	Calculated excitation energy (Ev)	Oscillator strength	UV(Monomer) (nm)
BP1	1	$n-\pi^*$	3.15	1.39	394.05
	2	$\pi-\pi^*$	4.51	0.082	275.07
	3	$\pi-\pi^*$	4.73	0.0001	261.94
	4	$n-\sigma^*$	5.07	0.0047	244.40
	5	$n-\pi^*$	5.10	0.15	243.10
BP2	1	$n-\pi^*$	3.11	1.57	398.47
	2	$\sigma-\pi^*$	4.51	0.075	274.89
	3	$\pi-\pi^*$	4.57	0.020	271.45
	4	$\sigma-\sigma^*$	5.09	0.14	243.73
	5	$\pi-\pi^*$	5.34	0.0007	232.01
BP3	1	$n-\pi^*$	3.10	1.6	400.54
	2	$\pi-\pi^*$	4.46	0.065	277.69
	3	$\sigma-\pi^*$	4.56	0.0033	271.82
	4	$\pi-\sigma^*$	5.10	0.13	242.95
	5	$\sigma-\sigma^*$	5.35	0.0009	231.86
BP4	1	$n-\pi^*$	3.12	1.58	397.65
	2	$\pi-\pi^*$	4.49	0.074	275.99
	3	$\sigma-\pi^*$	4.59	0.0005	270.07
	4	$\pi-\sigma^*$	5.12	0.11	242.34
	5	$\sigma-\sigma^*$	5.36	0.0005	231.40
BP5	1	$n-\pi^*$	3.21	1.57	386.27
	2	$\pi-\pi^*$	4.61	0.085	269.15
	3	$\sigma-\pi^*$	4.61	0.0031	266.15
	4	$\pi-\sigma^*$	5.19	0.11	239.12
	5	$\sigma-\sigma^*$	5.44	0.0005	227.79

from BP3 to BP5. The increase in the Dipole Moment is an indication that the centre of positive and negative charges are relatively bigger, while decrease in the Dipole Moment is an indication that they are closer. Further, this change in Dipole Moment is in line with the change in the experimentally available E_g values.

There is no significant effect of change in the Total Energy, Thermal Energy, Specific Heat Capacity and Entropy on the band/gap since they increase in value with the size of the system. The only nonlinear change is in the values of dipole. We therefore try to know the correlation of its change with the change in E_g values but found out to be very low with r^2 equal 0.199, which means is approximately only 20% relevant, which is very low compared to the correlation of the charges as observed previously. From multiple regressions, the relation can be expressed as:

$$E_g = 2.35 - 4.16E-03*B_8$$

The calculated values for the Total Energy, Thermal Energy, Specific Heat Capacity and Entropy by ROHF, SVWN, BLYP and B3LYP are relatively close in values.

Excited state properties

Table 7 shows the five single excited state for the different forms of squaraines considered. It is only BP1 that has a symmetry of C_s , all others have C_1 symmetry and all their states are A. The maximum absorption and maximum Oscillator Strength for each squaraines model are at the first excited state. The highest transition in each of the squaraines is $n-\pi^*$ transition and it is followed by $\pi-\pi^*$ and $\pi-\sigma^*$ transitions. Paterson et al. (2002) reported $n-\pi^*$ and $\pi-\pi^*$ transitions of another type of squaraines, but there is a reverse in our oscillator strength compared to their finding. The reason for this is the absent of lone-pair atom in their type of squaraines,

which make their $n-\pi^*$ transition a forbidden one.

The calculated values of UV are lower than the values reported in the literature (Ajayaghosh, 2003a, b; Arunkumar et al., 2006; Thomas et al., 1997; Jyothish et al., 2007; Law et al., 1986; Paterson et al., 2002) because the Monomers we used are just D-A unit compared to theirs, which were D-A-D unit. However, the trend of UV value is very significant to describe the change in the intrinsic conductivity.

The increase in the UV maximum absorption of the monomers from BP1 to BP3 shows the positive effect of increase in alkylation on the reduction of E_g values. The significant effect of steric hindrance, which resulted in increased E_g values from BP4 to BP5 is also reflected through the reduction in the UV maximum absorption.

The gradual increase in UV absorption maximal from BP1 to BP3 further adds meaning to reduction in calculated E_g values from BP1 to BP3.

The gradual drop in the UV absorption from BP4 to BP5 is also reflected from the calculated band-gap by ROHF functional, which shows a gradual increase in band-gap from BP4 to BP5. This is a reflection of the steric hindrance constituted by larger substituted alkyl groups on the nitrogen atoms (Figure 1). This steric effect is even more pronounced from the experimental band-gap as it starts increasing from BP3 and even though BP5 is a bit lower than BP4, which is still higher than BP2.

Conclusion

The Band-Gap Energy, DOS and IR Frequencies of squaraines BP1, BP2, BP3, BP4 and BP5 were calculated on the monomers and dimers using the *ab initio* Hartree-Fock, ROHF; Density Functional method BLYP and SVWN and Hybrid Functional B3LYP and their Excited State properties calculated on their monomers using CIS functional.

The results show that ROHF best reproduced the trend of change and the next to it is B3LYP. But B3LYP gave values that are much closer to the experimental values than the rest of the functional, while ROHF overestimated the values and BLYP and SVWN underestimated the E_g values.

From this, we can infer that though increase in alkylation, which is an electron releasing group will widen the width of HOMO and thereby reduce the band-gap, but at a certain level of alkylation, the steric hindrance will overrule the positive effect of alkylation and therefore results in increasing band-gap. The gradual increase in UV absorption from the BP1 to BP3 due to increase in alkylation is correlated with decrease in band-gap energy accordingly. The significant effect of steric hindrance from BP4 and BP5 that resulted to increase in band-gap is also reflected through decreasing values of their UV absorption.

More so, the trend of change in the intensity of DOS due to alkylation is significant. A decrease in band-gap

is accompanied with an increase in the intensity of DOS from monomers to dimers.

In addition, lower band gap is also with the higher value of IR maximum absorption.

This study showed that increasing the strength of electron releasing groups that are bonded to squaric unit by alkylation will enhance the quality of polysquaraines intrinsic conductivity. More so, further alkylation can constitute a steric hindrance, which will consequently lead to increase in energy band gap.

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