

# A comparative study of semi-squaraine and squaraine dyes using computational techniques: tuning the charge transfer/biradicaloid character by substitution

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**Abstract** Semi-squaraines (SMSQ) are known as donor-acceptor (D-A) type molecules whereas squaraines (SQ), which differs from SMSQ by an extra donor group, are more or less biradicaloids in nature. The effect of the additional donor group in SQ, which changes the nature of the molecule, on geometrical and electronic structure are studied here and compared with the corresponding SMSQ. It is noticed from the geometrical parameters that, a strong resonance exists in SQ whereas disparity in carbon-carbon bond lengths of central C<sub>4</sub> ring is seen in SMSQ dyes. The increasing and decreasing of antibonding interactions between central C<sub>4</sub> ring and side donor groups cause destabilization of HOMO and stabilization of LUMO respectively in case of SQ compared to SMSQ molecules. This leads to decreasing the HOMO-LUMO gap and promotes biradicaloid character of SQ. The absorption maxima obtained by using TD-DFT method with BLYP, B3LYP, BHandHLYP, CAM-B3LYP and M06-2X functionals are not in good agreement with experimental results. On the other hand SAC-CI method gives better results for all the molecules.

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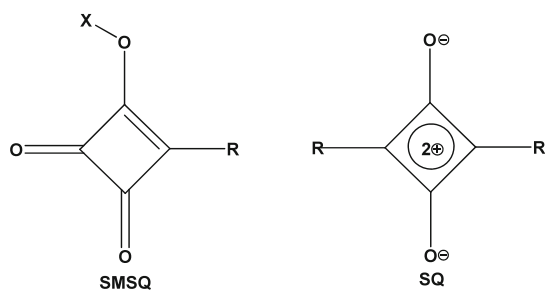
From this work we can evolve a design principle of these molecules which play a role as sensitizers in dye sensitized solar cells.

**Keywords** Biradicaloid character · SAC-CI · Squarylium dyes · TD-DFT

## Introduction

Ever since the first synthesis of squaraine (SQ) dyes was reported by Treibs and Jacob in 1965 [1], SQ dyes have been a novel class of organic dyes that play a crucial role in the development of various types of materials, which are used in nonlinear optics, electrophotography, xerography, photovoltaic, chemo sensors, biological labeling, and photodynamic therapy [2–37]. Synthesis of SQ dyes involves double nucleophilic attack over squaric acid. From the mechanistic point of view formation of SQ involves semi-squaraines (SMSQ) as intermediates (Scheme 1). These SMSQ are used as the precursors for synthesis of SQ, unsymmetrical squaraine (USQ) and core-substituted squaraine (CSQ) dyes [38–44]. On the other hand, SQ dye absorb in the near infrared (NIR) region 550 nm–900 nm while SMSQ have wide absorption spectrum coverage from 350 nm to 500 nm depending upon the side aromatic groups present [41, 45–47]. Recent research findings show that SMSQ have diverse applications such as sensitizers of TiO<sub>2</sub> semiconductor, potential scaffolds for divalent metal cations and effective inhibitors of protein tyrosine phosphatase [48–53].

SQ dyes are thought to be donor-acceptor-donor (D-A-D) type and assumed that the charge transfer (CT) takes place from the two side donor groups (aromatic moieties) to the central acceptor (C<sub>4</sub>O<sub>2</sub> ring) part. Many SQ derivatives are synthesised with different side -R donor group (to improve



Where X = H, CH<sub>3</sub>

**Scheme 1** Representative structures of SMSQ and SQ

the absorption properties) [3, 54–73]. Increasing electron donating ability of side groups, conjugation and solvent polarity does not show much effect in absorption [3, 74]. However SQ dyes on complexation with tetralactams have improved chemical stabilities, red-shifted absorption/emission maxima, and different cell localization propensities [75, 76]. Apart from that from the high-level *ab initio* theoretical studies it is clear that the charge transfer (CT) is very low and does not play a role in the NIR absorption of the SQ dyes but, the perturbation of the HOMO-LUMO gap (HLG) from both the geometry and substitution leads to the biradicaloid character (BRC) which is attributed to the NIR absorption [77, 78]. On the other hand, theoretical calculations on SMSQ revealed that these are pure D-A kind of molecules and during excitation, CT takes place from electron rich aromatic group centered HOMO to the semi-squarate centered LUMO [46, 48]. Hence, it remains a question that, by adding another –R group (which is a donor) to SMSQ (D-A) dyes, why the SQ dyes show biradicaloid nature instead of D-A-D character. In order to look into this, six SMSQ derivatives and corresponding six SQ derivatives have been considered to study the geometrical and electronic structural differences between these two classes of molecules.

### Computational methodology

The results of the calculations reported in this work have been obtained using the Gaussian 09 *ab initio*/DFT quantum chemical simulation package [79]. Experimentally reported six SMSQ molecules and corresponding six SQ molecules are investigated, which are shown in Fig. 1 [40, 41, 80, 81]. They are phenyl, pyrrole, indole, thiophene, benzothiazole and quinoline derivatives of SMSQ as SMSQ-B, SMSQ-P, SMSQ-N, SMSQ-T, SMSQ-BT and SMSQ-QN respectively and similarly SQ-B, SQ-P, SQ-N, SQ-T, SQ-BT and SQ-QN respectively for SQ derivatives. The gas phase optimization

of all the possible conformations of these molecules have been carried out using the hybrid density functional-B3LYP and Pople's split valence basis set with polarization and diffuse functions [6-311+G(d,p)] using the default integration grid as implemented in Gaussian 09 [82–84]. The obtained minimal configuration is further confirmed by the frequency calculation at the same level. From the population analysis, the individual contribution from each subgroup of molecule to the HOMO and LUMO is estimated at B3LYP/6-311G(d,p) level by using VMOdes Program [85].

The percent of BRC is estimated by using natural orbital occupation numbers method suggested by Nakano et al. [86]. It is related to the HOMO–i and LUMO+i and is defined as the weight of doubly excited configuration in the MC-SCF theory and is formally expressed in the spin-projected UHF (PUHF) theory as:

$$C_D = \left( 1 - \frac{2S_i}{1 + S_i^2} \right) \times 100. \quad (1)$$

Where,  $S_i$  is the orbital overlap ( $\chi_{HOMO-i}$  and  $\eta_{HOMO-i}$ ) between the corresponding pairs.

$$\chi_{HOMO-i} = \cos(\omega)\phi_{HOMO-i} + \sin(\omega)\phi_{LUMO+i}$$

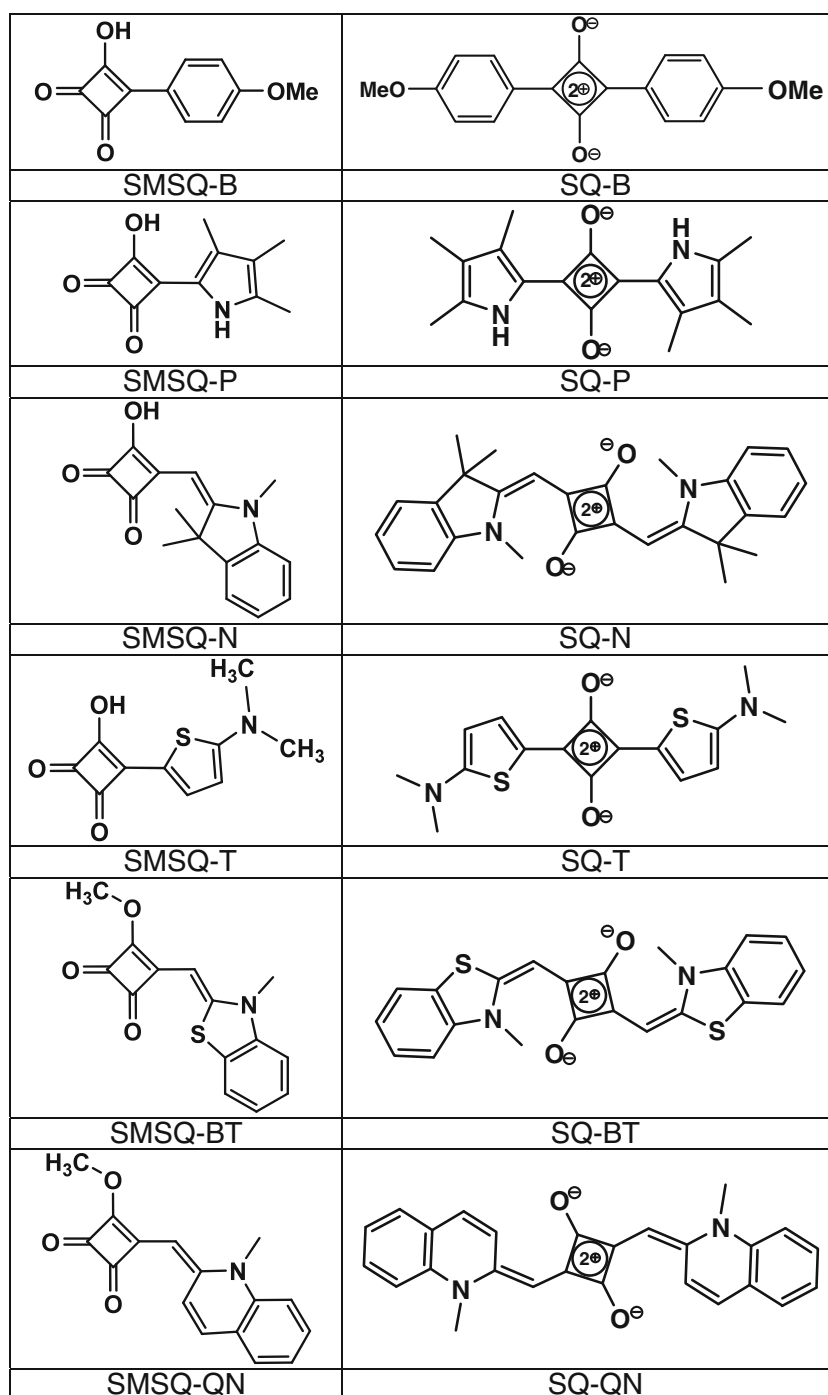
and

$$\eta_{HOMO-i} = \cos(\omega)\phi_{HOMO-i} - \sin(\omega)\phi_{LUMO+i}$$

Here  $\omega$  and  $\phi$  represent the UHF natural orbital (UNO) and orbital mixing parameter, respectively. The orbital overlap can be replaced by the occupation numbers ( $n_i$ ) of UNOs, which are obtained from the density matrix. This has been shown to be suitable. Therefore  $S_i$  can be expressed as

$$S_i = \frac{n_{HOMO-i} - n_{LUMO+i}}{2}.$$

To obtain the adiabatic singlet-triplet gap (STG), the lowest singlet geometries have been considered as the initial geometries for calculating the lowest triplet state geometries at the UB3LYP/6-311+G(d, p) level of theory. The singlet geometries obtained are subjected to TD-DFT (with different functional and basis sets in gas and solvent phases) and SAC/SAC-CI/6-311g(d,p) calculations to study the singlet-singlet transition. The effect of solvent on excitation energies has been studied by polarizable continuum model (PCM) in the TD-DFT calculations [87]. The SAC method is based on the spin and space adapted formalism of the cluster expansion methods and the detailed methodology of this is given elsewhere [88, 89]. Due to the large size of SQ molecules active space of 170 to 190 orbitals is chosen with the window option in SAC/SAC-CI calculation whereas full window has been considered for SMSQ molecules. The SAC-CI is also restricted to singles and doubles linked operators, while the higher order ones are treated through

**Fig. 1** Molecules considered in this study

unlinked operators. Four lowest excited states for each irreducible representation of each molecule are obtained.

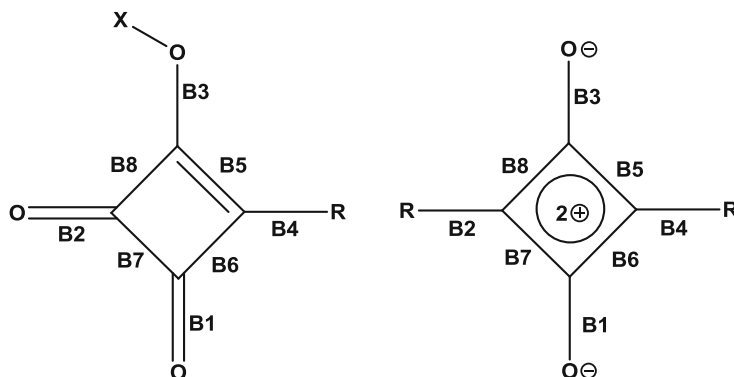
## Results and discussion

### Geometries

The selected geometrical parameters for all molecules obtained at B3LYP/6-311+G(d,p) level are given in Table 1

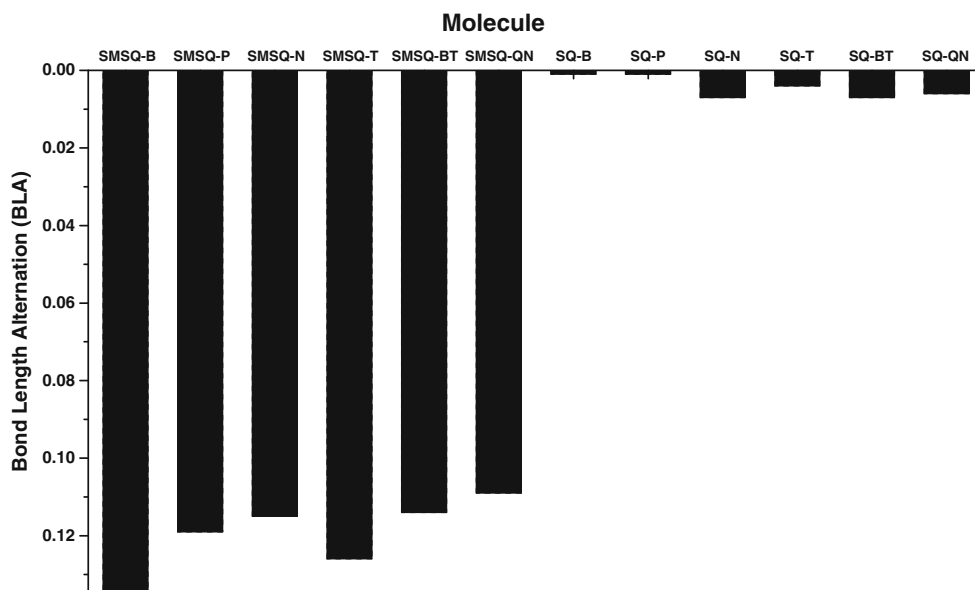
and are in good agreement with the available experimental data for SMSQ-QN, SQ-N, SQ-BT and SQ-QN molecules [73, 90]. The C = O bond lengths of two carbonyl groups B1 and B2 are found to be similar in all SMSQ molecules. The maximum difference obtained is 0.006 Å for SMSQ-T. The C-O bond length, B3 is minimum 1.322 Å for SMSQ-QN and maximum 1.330 Å for both SMSQ-N and SMSQ-T. On the other hand, bond length between central ring and side – R group is different in all SMSQ which is between 1.407 Å (SMSQ-T) and 1.437 Å (SMSQ-B). The carbon-carbon

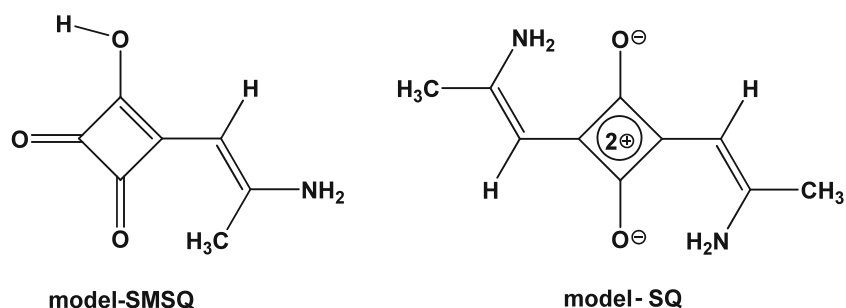
**Table 1** Optimized geometrical parameter (bond lengths in Å), symmetry point group (PG) for all molecules obtained at B3LYP/6-311+G(d,p) level. Available X-ray data for SMSQ-QN, SQ-N, SQ-BT and SQ-QN are given in parentheses



Molecule	PG	B1	B2	B3	B4	B5	B6	B7	B8
SMSQ-B	C <sub>s</sub>	1.202	1.203	1.326	1.437	1.381	1.503	1.556	1.485
SMSQ-P	C <sub>1</sub>	1.208	1.207	1.329	1.409	1.388	1.499	1.546	1.476
SMSQ-N	C <sub>1</sub>	1.204	1.209	1.330	1.418	1.393	1.517	1.543	1.465
SMSQ-T	C <sub>1</sub>	1.201	1.207	1.330	1.407	1.386	1.508	1.552	1.475
SMSQ-BT	C <sub>1</sub>	1.205	1.209	1.323	1.411	1.395	1.501	1.546	1.480
SMSQ-QN	C <sub>1</sub>	1.208 (1.209)	1.210 (1.226)	1.322 (1.315)	1.412 (1.401)	1.399 (1.408)	1.506 (1.501)	1.541 (1.515)	1.476 (1.457)
SQ-B	C <sub>2h</sub>	1.223	1.414	1.223	1.414	1.474	1.475	1.474	1.475
SQ-P	C <sub>i</sub>	1.230	1.392	1.230	1.392	1.469	1.470	1.469	1.470
SQ-N	C <sub>2h</sub>	1.228 (1.240)	1.399 (1.399)	1.228 (1.240)	1.399 (1.399)	1.472 (1.464)	1.479 (1.466)	1.472 (1.464)	1.479 (1.466)
SQ-T	C <sub>2</sub>	1.223	1.389	1.223	1.389	1.472	1.476	1.472	1.476
SQ-BT	C <sub>2h</sub>	1.228 (1.230)	1.395 (1.398)	1.228 (1.235)	1.395 (1.398)	1.472 (1.466)	1.479 (1.468)	1.472 (1.466)	1.479 (1.468)
SQ-QN	C <sub>i</sub>	1.229 (1.226)	1.393 (1.397)	1.229 (1.226)	1.393 (1.397)	1.472 (1.466)	1.478 (1.485)	1.472 (1.466)	1.478 (1.485)

**Fig. 2** The bond length alternation (BLA in Å) calculated for all molecules



**Scheme 2** Model molecules considered in this study

bond lengths in central C4 ring are different for all SMSQ molecules. The bonds B5 and B7 are the shorter and longer carbon-carbon bonds respectively while B6 and B8 are intermediate to them. The bond lengths are less than 1.400 Å for B5 which shows larger bond order character. At the same time B7 is more than 1.541 Å and up to 1.556 Å corresponding to single bond behavior. In between B6 and B8, shorter bond lengths are obtained for the latter.

In the case of SQ molecules, two carbonyl C = O bond lengths are larger than in respective SMSQ molecules. Both C = O bonds are symmetrically equivalent as well as other carbon-carbon bonds. In general, bond lengths between central ring and side -R groups are shorter in SQ than respective SMSQ molecule. This shows stronger conjugation between central ring and side -R groups in SQ than SMSQ. The bond lengths B2 and B4 are found to be in between 1.223 Å and 1.230 Å. On the other hand, the inequality in carbon-carbon bond lengths in central C4 ring of SMSQ mol-

ecules is removed in SQ. The opposite side bonds B5, B7 and B6, B8 are equivalent. Moreover these two pairs of bond lengths are not much different from each other and show 0.001 Å and 0.007 Å of minimum and maximum difference in the case of SQ-B, SQ-P and SQ-N, SQ-BT respectively.

The bond length alternation (BLA) is an important geometrical parameter which can be used to define the electron delocalization in  $\pi$ -conjugated systems [91–96]. This is the difference between consecutive carbon-carbon single bonds and double bonds in the conjugated system. The bond lengths B6, B7 and B8 are considered as single bonds and B5 as double bond for all SMSQ molecules. In the case of SQ, the bond lengths B5, B7 and B6, B8 are considered as double bonds and single bonds respectively in the central C4 ring even though there is not much difference among them. By using the following equations the estimated BLA within the central C4 ring of all the molecules is given in Fig. 2.

**Fig. 3** Frontier molecular orbitals of model-SMSQ, model-SQ, SMSQ-N and SQ-N molecules

Molecule	HOMO	LUMO
Model-SMSQ		
Model-SQ		
SMSQ-N		
SQ-N		

$$BLA(SMSQ) = B5 - (B6 + B7 + B8)/3$$

$$BLA(SQ) = (B5 + B7)/2 - (B6 + B8)/2$$

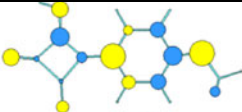
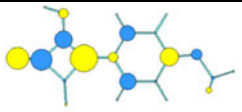

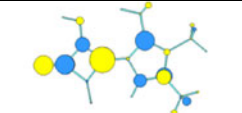

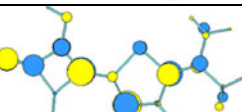
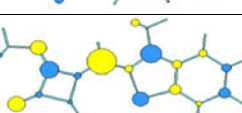
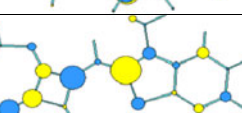
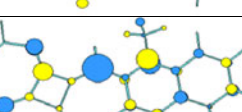
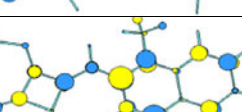
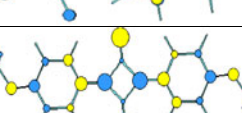
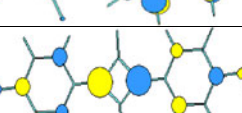
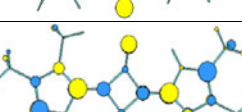
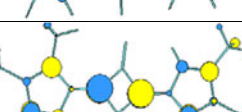
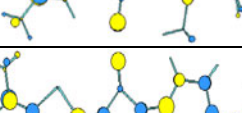
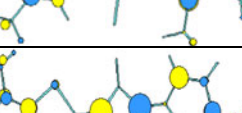
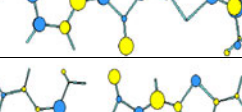
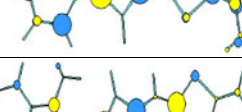
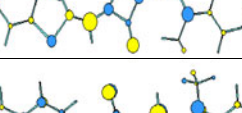
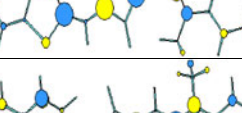
It is seen from Fig. 2 that the BLA is quite large in SMSQ molecules. The maximum and minimum values 0.134 Å and 0.109 Å obtained for SMSQ-B and SMSQ-QN respectively showing large disparity between carbon-carbon single bonds and double bond. In contrast, for SQ the BLA values are found to be negligible when compared to respective SMSQ molecules. This enables the strong resonance in central C4 ring of

all SQ molecules than in corresponding SMSQ.

Frontier molecule orbital analysis and biradicaloid character

The major structural difference between SMSQ and SQ is that, SQ has two-R groups and SMSQ has one –R group substituted to central C4 ring (Fig. 1). NIR absorption of SQ dyes is attributed to the oxyallyl substructure which is a non-kekule biradicaloid moiety [77, 78, 97–103]. To understand the effect of this –R group on the BRC and HLG of SQ molecules a detailed analysis of frontier orbitals (HOMO and LUMO) has been carried out. For this purpose two model molecules have been considered as model-SMSQ and model-SQ which are

**Fig. 4** Frontier molecular orbitals of all other SMSQ and SQ molecules

Molecule	HOMO	LUMO
SMSQ-B		
SMSQ-P		
SMSQ-T		
SMSQ-BT		
SMSQ-QN		
SQ-B		
SQ-P		
SQ-T		
SQ-BT		
SQ-QN		

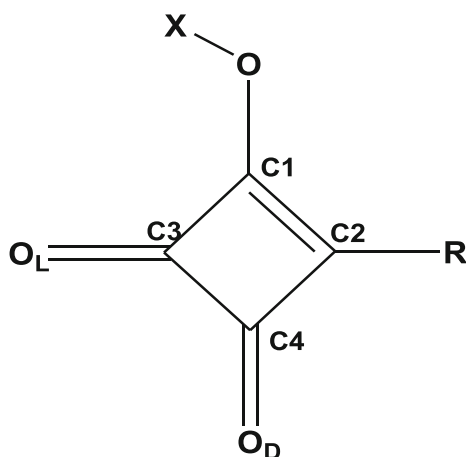
given in Scheme 2. They resemble SMSQ and SQ molecules respectively. For the sake of clarity, the frontier molecular orbitals of two model molecules and representative SMSQ-N and SQ-N are given in Fig. 3 while frontier molecular orbitals of all other molecules are given in Fig. 4.

These figures make it clear that orbital pictures of model molecules are very similar when compared with SMSQ and SQ. The difference between model-SMSQ and model-SQ is seen with the localization of orbital lobes on central ring. In the case of HOMO of model-SMSQ, the noticeable contribution is only from C1 which has antibonding interaction with oxygen from –OH group. While in model-SQ, both C2 and C3 show antibonding interaction with carbon of side –R groups ( $C_R$  &  $C_L$ ). In the case of LUMO of model-SMSQ, a small lobe on C1 has bonding and antibonding interactions with C3 and C2 respectively whereas C3 and –O of C = O

(left carbonyl group) have strong antibonding interaction, but for model-SQ, C2 and C3 show non-bonding nature.

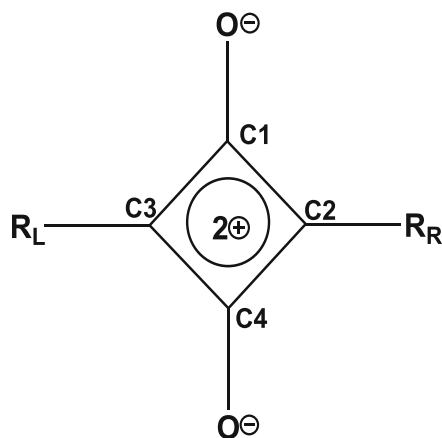
In order to understand the effect of these bonding, antibonding and non-bonding interactions on the orbital energy levels, systematic population analysis has been done and the results are given in Tables 2 and 3 for SMSQ and SQ respectively. In the HOMO of model-SMSQ, the antibonding percentage of C1 and oxygen of –OH group is 13.1 % and 9.5 % respectively. However, in HOMO of model-SQ, the two antibonding interactions between central ring and carbon of side –R groups ( $C_L/C_R$ ) are observed with 6.7 % and 14.0 % of each. The increased antibonding characters lead to destabilization of HOMO. This is seen from Fig. 5 that the HOMO of model-SMSQ is at –5.78 eV while for model-SQ it is at –4.83 eV. In the case of LUMO of model-SMSQ, the antibonding nature between C1, C2 and C3, –O

**Table 2** Population analysis (%) of all SMSQ molecules obtained at B3LYP/6-311G (d,p) level



#### Semi-squaraine molecules

Molecule	Orbital	Central	Central C <sub>4</sub>				R		O <sub>L</sub>	O <sub>D</sub>	OX
			C1	C2	C3	C4	Total	C <sub>R</sub>			
Model-SMSQ	HOMO	18.9	13.1	3.2	1.6	1.0	55.7	25.0	10.7	5.2	9.5
	LUMO	40.8	6.2	20.7	13.4	0.5	43.8	0.9	13.6	0.2	1.6
SMSQ-B	HOMO	14.9	9.9	3.3	1.0	0.6	66.1	16.3	7.2	4.0	7.8
	LUMO	47.0	9.8	22.4	14.3	0.4	35.0	3.0	15.1	0.1	2.8
SMSQ-P	HOMO	15.0	11.1	1.3	1.6	1.0	65.2	24.6	8.9	3.4	7.4
	LUMO	47.4	8.7	24.2	14.2	0.3	35.9	0.5	14.4	0.0	2.3
SMSQ-N	HOMO	12.2	8.9	1.0	1.4	1.0	71.9	20.6	7.5	2.8	5.5
	LUMO	37.4	6.9	18.6	11.4	0.4	48.3	1.2	12.3	0.2	1.8
SMSQ-T	HOMO	11.5	8.8	0.7	1.4	0.7	73.6	19.3	6.8	2.3	5.8
	LUMO	35.3	7.3	17.1	10.5	0.4	51.0	2.5	11.4	0.1	2.1
SMSQ-BT	HOMO	13.4	9.5	1.6	1.6	0.7	66.7	23.1	8.1	3.8	8.0
	LUMO	34.3	7.0	16.8	10.0	0.4	52.5	1.4	11.1	0.1	2.0
SMSQ-QN	HOMO	14.4	10.2	1.5	1.8	1.0	64.3	24.2	9.0	3.9	8.3
	LUMO	17.9	4.4	7.7	5.4	0.4	73.8	4.0	6.7	0.3	1.4

**Table 3** Population analysis (%) of all SQ molecules obtained at B3LYP/6-311G (d,p) level

## Squaraine molecules

Molecule	Orbital	Central	Central C <sub>4</sub>				R <sub>L</sub>		R <sub>R</sub>		2O
			C1	C2	C3	C4	Total	C <sub>L</sub>	Total	C <sub>R</sub>	
Model-SQ	HOMO	17.3	1.9	6.7	6.7	1.9	31.5	14.0	31.5	14.0	19.7
	LUMO	38.0	0.1	18.9	18.9	0.1	31.0	1.1	31.0	1.1	0.0
SQ-B	HOMO	20.9	1.2	9.2	9.2	1.2	26.9	6.1	26.9	6.1	25.4
	LUMO	47.7	0.1	23.7	23.7	0.1	26.2	0.1	26.2	0.1	0.0
SQ-P	HOMO	15.4	1.7	6.0	6.0	1.7	33.8	11.6	33.8	11.6	17.0
	LUMO	40.8	0.1	20.3	20.3	0.1	29.6	0.7	29.6	0.7	0.0
SQ-N	HOMO	14.6	1.6	5.7	5.7	1.6	35.0	10.9	35.0	10.9	15.5
	LUMO	33.0	0.1	16.4	16.4	0.1	33.5	0.4	33.5	0.4	0.0
SQ-T	HOMO	13.8	1.3	5.6	5.6	1.3	35.6	8.9	35.6	8.9	15.0
	LUMO	32.2	0.1	16.0	16.0	0.1	33.9	0.2	33.9	0.2	0.0
SQ-BT	HOMO	13.6	1.6	5.2	5.2	1.6	36.2	11.5	36.2	11.5	14.1
	LUMO	29.3	0.1	14.6	14.6	0.1	35.4	0.5	35.4	0.5	0.0
SQ-QN	HOMO	14.6	1.6	5.7	5.7	1.6	34.9	11.2	34.9	11.2	15.5
	LUMO	21.9	0.0	10.9	10.9	0.0	39.0	0.1	39.0	0.1	0.0

(left) are with contributions 6.2 %, 20.7 % and 13.4 %, 13.6 % respectively. It also shows that the bonding nature of C1 and C3 is less prominent and nonbonding nature at C2 and C3 (18.9 % on each) in model-SQ leads to stabilization of LUMO. From Fig. 5, the LUMO of model-SMSQ and model-SQ are at  $-1.71$  eV and  $-2.29$  eV respectively. Hence HLG in model-SQ is estimated as  $-2.29$  eV which is smaller than in model-SMSQ ( $-4.07$  eV). The destabilization of HOMO and stabilization of LUMO for all SQ molecules with respect to their SMSQ molecules is shown in Fig. 5. Hence the HLG of SQ molecules are smaller than respective SMSQ molecules.

Fabian and Zahradnik had successfully brought up the structure-color relationship of dyes and classified some of the molecules as biradicaloid dyes [43, 44]. The larger wavelength absorption of such dyes is attributed to the biradicaloid

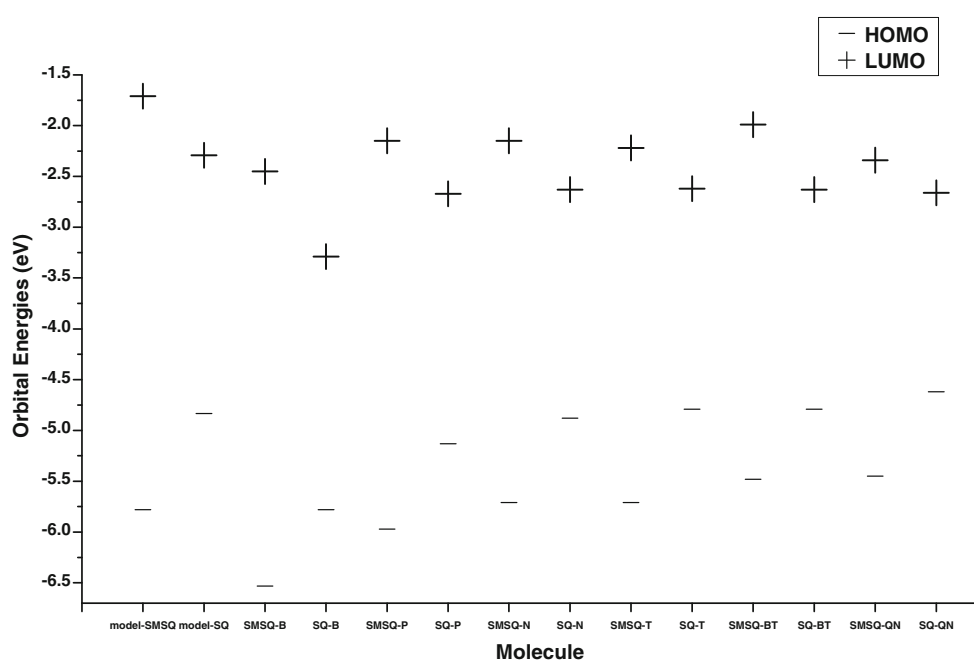
nature, indicating smaller HLG. This enables the BRC in SQ. Several methods have been suggested for estimating the BRC character. Wirz had suggested that a molecule can be said to be a biradicaloid if the splitting between the singlet ( $S_0$ ) and triplet ( $T_1$ ) is around  $2-24$  kcal mol<sup>-1</sup> [104].

From Table 4, all SMSQ molecules have high STG values and hence very low BRC. Whereas four SQ molecules have STG around  $24$  kcal mol<sup>-1</sup>, and SQ-B and SQ-P have  $27.26$  kcal mol<sup>-1</sup> and  $26.95$  kcal mol<sup>-1</sup> respectively. Hence these molecules can be considered as borderline biradicaloid molecules.

It has been found in earlier studies that BRC estimated by the unrestricted DFT methods is underestimated whereas the *ab initio* UHF methods give reasonable BRC [105, 106]. The values estimated from UHF method are 19.96, 18.46 and 20.71 respectively for SQ-B, SQ-P and SQ-T, but SQ-



**Fig. 5** Frontier molecular orbital energy levels (HOMO and LUMO) of all SMSQ and SQ molecules



N, SQ-BT and SQ-QN show low BRC values 9.96, 9.42 and 13.56 respectively. This is attributed to the extension of  $\pi$ -conjugation which is increased in these three molecules. The spin density distribution analysis has been done and given in supporting information (Table S3). It is seen from this table that the spin density is delocalized over the molecule which is in agreement with the borderline BRC of SQ molecules.

The wave function stability analysis has been carried out [107, 108]. Here it is seen that there is no external instability

in the wave function in agreement with the earlier reports for SQ dyes [100].

#### SAC/SAC-CI study

##### Calculation of absorption maxima

Absorption maxima obtained by TD-DFT with different functional like BLYP, B3LYP, BHandHLYP, CAM-B3LYP

**Table 4** HOMO-LUMO gap (HLG in eV), BRC (%), singlet-triplet gap (STG in kcal mol<sup>-1</sup>), and eigen values of the stability matrix of all SMSQ and SQ molecules

Molecule	HLG	BRC	STG	Eigen value
model-SMSQ	-4.07	0.08	-41.79	0.0645
model-SQ	-2.54	5.86	-17.85	0.0254
SMSQ-B	-4.08	1.94	-55.81	0.0702
SMSQ-P	-3.82	1.02	-50.05	0.0636
SMSQ-N	-3.56	0.13	-48.41	0.0605
SMSQ-T	-3.48	1.81	-45.78	0.0567
SMSQ-BT	-3.49	0.21	-47.18	0.0600
SMSQ-QN	-3.12	1.06	-39.97	0.0491
SQ-B	-2.49	19.96	-27.26	0.0252
SQ-P	-2.46	18.46	-26.95	0.0263
SQ-N	-2.25	9.96	-24.41	0.0225
SQ-T	-2.17	20.71	-22.95	0.0204
SQ-BT	-2.16	9.42	-24.48	0.0241
SQ-QN	-1.95	13.56	-20.98	0.0195

**Table 5** Absorption maxima ( $\lambda_{\max}$  in nm), oscillator strength ( $f$ ), TDM ( $\mu_{ge}$ ), ground ( $\mu_g$ ) and excited state ( $\mu_e$ ) dipole moment (in Debye) of all SMSQ and SQ molecules obtained at SAC/SAC-CI/6-311g(d,p) level

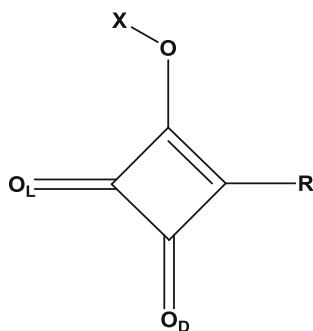
Molecules	$\lambda_{\max}^a$	$f$	$\mu_{ge}$	$\mu_g$	$\mu_e$
SMSQ-B	326(333)	0.836	7.62	4.92	10.53
SMSQ-P	365(378)	0.791	7.84	4.82	8.65
SMSQ-N	428(422)	0.787	8.46	6.70	11.81
SMSQ-T	409(425)	0.770	8.19	8.19	13.20
SMSQ-BT	418(442)	0.885	8.86	8.16	12.54
SMSQ-QN	454(465)	0.913	9.39	7.78	10.86
SQ-B	534(540)	1.119	11.28	0	0
SQ-P	563(565)	1.291	12.43	0	0
SQ-N	639(635)	1.355	13.57	0	0
SQ-T	642(654)	1.317	13.41	0	0
SQ-BT	685(685)	1.519	14.86	0	0
SQ-QN	716(715)	1.567	15.45	0	0

<sup>a</sup> Experimental absorption maxima ( $\lambda_{\max}$ ) has been given in parentheses

and M06-2X using various basis sets for both gas phase and solvent phase are given in supporting information (Table S1). It is seen that the results obtained using TD-DFT are blue shifted and do not match with experimental results [76, 101, 109]. From Table S1 it is seen that the hybrid functionals B3LYP and BHandHLYP show 100–125 nm and 70–93 nm deviation in gas phase and solvent phases respectively for SQ molecules while up to 82 nm and 63 nm for SMSQ molecules in gas phase and solvent phases respectively. Similarly the more recent functionals CAM-B3LYP and M06-2X also show more than 100 nm and 70 nm for SQ molecules while 71 nm and 52 nm for SMSQ molecules for gas phase and solvent phases respectively. The pure DFT functional BLYP has shown large average deviation for SQ and small deviations are seen for SMSQ, but the deviations for individual molecules are considerably large for all the functionals. From Table S2 (in supporting information) it is

also seen that the singlet ground state of SMSQ and SQ molecules is largely contributed by a huge number of configurations and linked operators. Hence the multi-determinant treatment is required and therefore results obtained by TD-DFT methods are not in good agreement with experimental absorption maximum of SMSQ and SQ molecules. The SAC/SAC-CI technique has been used earlier for the oxyallyl substructure based dyes with success (a difference of less than 0.1 eV with the experimental observed excitation energy was obtained) [77, 78, 97–103], hence it has become the choice for this study also. The absorption maxima including oscillator strength, transition dipole moment (TDM), ground and excited state dipole moments obtained by SAC/SAC-CI method are shown in Table 5 for all the molecules. It is seen from this table that the results obtained at SAC/SAC-CI method are in good agreement with experimentally determined results [40, 41, 80, 81].

**Table 6** Charge transfer (in  $e$ ) data of all SM-SQ molecules from ground ( $S_0$ ) to excited ( $S_1$ ) state obtained at SAC/SAC-CI/6-311G (d,p) level



R = side substituent (Figure1)

OX where X= H, CH<sub>3</sub> (Figure1)

C<sub>4</sub> = central 4 carbons

O<sub>L</sub> = oxygen on left side

O<sub>D</sub> = oxygen on down side

Molecule	$Q/e$	O <sub>L</sub>	O <sub>D</sub>	OH/X	C <sub>4</sub> ring	R
SMSQ-B	$(Q/e)_{Gr}$	-0.366	-0.374	-0.130	0.733	0.137
	$(Q/e)_{Ex}$	-0.446	-0.397	-0.124	0.580	0.387
	$\Delta Q/e$	-0.080	-0.023	0.006	-0.153	0.250
SMSQ-P	$(Q/e)_{Gr}$	-0.386	-0.397	-0.136	0.635	0.284
	$(Q/e)_{Ex}$	-0.441	-0.423	-0.129	0.485	0.507
	$\Delta Q/e$	-0.055	-0.026	0.007	-0.150	0.223
SMSQ-N	$(Q/e)_{Gr}$	-0.402	-0.395	-0.140	0.739	0.197
	$(Q/e)_{Ex}$	-0.462	-0.422	-0.140	0.574	0.451
	$\Delta Q/e$	-0.060	-0.027	-0.001	-0.166	0.254
SMSQ-T	$(Q/e)_{Gr}$	-0.386	-0.366	-0.135	0.786	0.101
	$(Q/e)_{Ex}$	-0.444	-0.404	-0.137	0.680	0.305
	$\Delta Q/e$	-0.057	-0.039	-0.001	-0.106	0.204
SMSQ-BT	$(Q/e)_{Gr}$	-0.401	-0.388	-0.138	0.717	0.210
	$(Q/e)_{Ex}$	-0.476	-0.405	-0.132	0.563	0.450
	$\Delta Q/e$	-0.075	-0.017	0.006	-0.154	0.241
SMSQ-QN	$(Q/e)_{Gr}$	-0.408	-0.404	-0.138	0.702	0.248
	$(Q/e)_{Ex}$	-0.456	-0.427	-0.141	0.660	0.364
	$\Delta Q/e$	-0.048	-0.023	-0.003	-0.041	0.116

$\Delta Q/e$  = [excited state charge — ground state charge]

SQ molecules absorb in longer wavelength region than the respective SMSQ molecules. The absorption values of both SMSQ and SQ molecules are given in the ascending order. In the case of SMSQ, the minimum and maximum absorptions are 333 nm and 465 nm for SMSQ-B and SMSQ-QN respectively, whereas for SQ they are obtained at 540 nm and 715 nm for SQ-B and SQ-QN respectively.

In the same way, TDM values are gradually increased from SMSQ-B to SMSQ-QN and SQ-B to SQ-QN, and also they are higher for SQ than SMSQ. Since the oscillator strength is a function of excitation energy and transition moment, larger oscillator strengths have been found for SQ than SMSQ. The ground and excited state dipole moments are obtained for SMSQ, but due to symmetry they are not found in parent SQ. By comparing the dipole moments it is seen that the excited state dipole moments are larger than ground state values. This corresponds to greater charge separation in excited state than in ground state of all SMSQ molecules. The transition moments are aligned through major axis of the molecule, while ground and excited state dipole moments are both in major and minor axis.

#### Charge transfer analysis

As per definition, in SAC studies, the HF contribution is 1.00 to the ground state. The HF ground state of all molecules is improved by SAC and small but reasonable contributions from excited states. Though the contribution from excited state electronic configuration is not high for both SMSQ and SQ which is up to 6 % and 10 % respectively, selective excited state configurations (coefficients of >0.05) are given in supporting information. The major contributions (mixing coefficient >0.07) to the excited states obtained by SAC-CI method are given in the same table. The major transition is from HOMO-LUMO single excitation which contributes more than 93 % and 94 % for SMSQ and SQ respectively. This facilitates the CT interactions between central ring and side -R groups. Apart from that double transitions also contribute to the excited state.

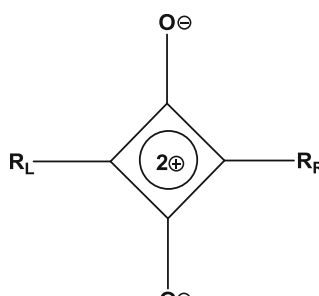
In order to understand the charge delocalization in both ground and lowest energy excited states, CT data has been compiled for absorption maxima for all molecules and given in Tables 6 and 7 for SMSQ and SQ respectively. This is based on the Mulliken charges obtained at SAC and SAC-CI levels respectively for ground and excited states. For convenience, the molecule is divided into groups. In the case of SMSQ, they are side -R group (substituent), -O<sub>L</sub> (left oxygen), -O<sub>D</sub> (down oxygen), -OX and central C<sub>4</sub> ring. For all these groups the net charge in both ground and excited states has been estimated. The difference between excited state charge and ground state charge gives the net charge gain or loss of the particular group.

From Table 6, it is clear that there is strong CT in SMSQ molecules. Major CT is from -R group to C<sub>4</sub> carbons, oxygens on left and down side of the molecule, i.e., -R group is

donor and C<sub>4</sub> carbons, oxygens on left and down side of the molecule are acceptors. In SMSQ-N, -R group donates 0.254e charge, which is gained by central C<sub>4</sub> ring (0.166e), -O<sub>L</sub> (0.060e) and -O<sub>D</sub> (0.027). In the case of SMSQ-QN, comparatively small charge is lost by -R group (0.116e) and charge gain is 0.048e and 0.041e by -O (left) and central C<sub>4</sub> ring respectively. Similar observations have been found in all other SMSQ molecules.

The CT data of SQ molecules has been given in Table 7. As in SMSQ, SQ is divided into side -R groups, two -O atoms and central C<sub>4</sub> ring groups. The difference between SMSQ and SQ with respect to charge delocalization is revealed from this table. In an analogous manner with earlier reports on symmetrical and unsymmetrical SQ molecules, in SQ molecules a small CT from side -R groups to the central C<sub>4</sub> ring has been found [97–103]. The net charge transition from side -R groups estimated is 0.068e, 0.061e and 0.042e for SQ-B, SQ-BT and SQ-QN respectively with 0.073e and 0.003e and

**Table 7** Charge transfer (in *e*) data of all SQ molecules from ground (S<sub>0</sub>) to excited (S<sub>1</sub>) state obtained at SAC/SAC-CI/6-311G (d,p) level



Molecule	<i>Q/e</i>	R <sub>L</sub>	R <sub>R</sub>	2O	C <sub>4</sub> ring
SQ-B	( <i>Q/e</i> ) <sub>Gr</sub>	0.180	0.180	-0.926	0.567
	( <i>Q/e</i> ) <sub>Ex</sub>	0.203	0.203	-0.853	0.448
	Δ <i>Q/e</i>	0.023	0.023	0.073	-0.119
SQ-P	( <i>Q/e</i> ) <sub>Gr</sub>	0.262	0.262	-0.991	0.467
	( <i>Q/e</i> ) <sub>Ex</sub>	0.274	0.274	-1.000	0.452
	Δ <i>Q/e</i>	0.011	0.011	-0.009	-0.014
SQ-N	( <i>Q/e</i> ) <sub>Gr</sub>	0.212	0.212	-1.011	0.586
	( <i>Q/e</i> ) <sub>Ex</sub>	0.246	0.246	-1.014	0.522
	Δ <i>Q/e</i>	0.034	0.034	-0.003	-0.064
SQ-T	( <i>Q/e</i> ) <sub>Gr</sub>	0.126	0.126	-0.927	0.676
	( <i>Q/e</i> ) <sub>Ex</sub>	0.149	0.149	-0.928	0.630
	Δ <i>Q/e</i>	0.024	0.024	-0.001	-0.046
SQ-BT	( <i>Q/e</i> ) <sub>Gr</sub>	0.239	0.239	-1.002	0.523
	( <i>Q/e</i> ) <sub>Ex</sub>	0.270	0.270	-0.999	0.459
	Δ <i>Q/e</i>	0.031	0.031	0.003	-0.065
SQ-QN	( <i>Q/e</i> ) <sub>Gr</sub>	0.652	0.652	-1.013	0.398
	( <i>Q/e</i> ) <sub>Ex</sub>	0.673	0.673	-0.994	0.339
	Δ <i>Q/e</i>	0.021	0.021	0.019	-0.059

$$\Delta Q/e = [\text{excited state charge} - \text{ground state charge}]$$

0.019e of charge donated by two –O atoms of the same molecules. In SQ the central C<sub>4</sub> ring is a mild acceptor which gains little charge in comparison to SMSQ molecules. In the case of SQ-P, SQ-N and SQ-T, there is no charge donation observed from the two –O atoms, and the overall charge donated by side –R groups is gained by central C<sub>4</sub> ring.

## Conclusions

The comparative study of donor-acceptor (D-A) type of six SMSQ and corresponding biradicaloid SQ molecules has been carried out in this work. The geometrical dissimilarity between SMSQ and SQ has been observed. The carbon-carbon bonds in central C<sub>4</sub> ring of SMSQ are different from each other whereas in SQ they are almost similar. Strong conjugation between electronic rich aromatic group (–R) and central C<sub>4</sub> ring is seen in SQ. The geometrical difference between SMSQ and SQ arises due to the second –R group. This additional –R group results in small HLG in SQ. In order to get more details, two model molecules are considered and population analysis of them is carried out. From this analysis and frontier molecular orbital pictures, it is found that more anti-bonding character between central ring and side –R groups destabilize the HOMO level in SQ while due to absence of such character and non-bonding character, LUMO is stabilized. Hence small HLG has been found in all SQ molecules compared with SMSQ molecules. This is very much consistent with BRC values obtained in which more BRC is found for SQ compared to the negligible values of SM-SQ. Absorption maxima obtained by using TD-DFT method with BLYP, B3LYP, BHandHLYP, CAM-B3LYP and M06-2X functionals are not in agreement with experimental results. However, SAC/SAC-CI results are in good agreement with experimentally obtained absorption values. The CT data obtained by SAC/SAC-CI studies shows that SM-SQ are D-A type of molecules where side –R groups are a donor while in SQ the extent of CT is less. We also see that SAC/SAC-CI method works better than TD-DFT methods even for D-A type molecules like SMSQ.

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