#### ORIGINAL PAPER



# A theoretical study of structural, opto-electronic and nonlinear properties of arylboroxine derivatives

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Received: 25 January 2017 / Accepted: 23 May 2017

Abstract: Density functional theory at CAM-B3LYP/6-311G++ (2d, 2p) level was employed to study the Triphenylboroxine derivatives (**TB**) containing electron donating and electron substituents, for their charge transfer and nonlinear optical properties. The results reveal that electron donating groups facilitate the rapid electron injection as compared to unsubstituted **TB**. It was observed that upon substitution with electron donating groups, the **TB** derivatives show an increased double bond character in the  $B_3$ - $C_{18}$  bond indicating an increase in the degree of conjugation. The Frontier molecular orbital studies indicate that highest occupied molecular orbitals of the neutral molecules delocalize primarily over the three phenyl rings and bridging oxygen atoms, whereas the lowest unoccupied molecular orbitals localize largely on the two phenyl rings and the boron atoms. Further, the TD-DFT studies indicate that the maximum absorption band results from the electron transitions from the initial states that are contributed by the HOMO and HOMO-1 to the final states that are mainly contributed by the LUMOs. In addition, we have observed that the introduction of electron donating group to the **TB-7** leads to more active nonlinear performance.

Keywords: Reorganization energy; Octupolar molecules; Polarizability; Hyperpolarizability; Hammett parameter

PACS No.: 61.66.Hq; 31.15.E-; 34.70.+e; 42.65.-k; 42.79.Kr; 71.90.+q; 05.45.-a

# 1. Introduction

Boroxine is inorganic analogue and isoelectron of benzene, share many similarities with it, both in structure and characteristics [1–3]. These are six membered cyclotrimeric anhydrides of organoboronic acids [R–B(OH)<sub>2</sub>] and the most stable forms of R–BO polymers [4]. During the last two decades several studies have been performed for their preparation, geometrical structures and electronic characteristics [1–4]. Boroxine became spotlight when Yaghi et al. [5] synthesized and characterized the crystalline arylboroxine-based covalent organic framework (COF-1) material. Boroxines have found commercial use in diverse areas such as flame retardant materials [6, 7], lithium ion transference in polymer electrolytes [8, 9], molecularly imprinted polymers for biosensor applications [10], nonlinear optical materials [11–14] and curing agents with encapsulants for solid state devices that function as optoelectronic devices [15]. They are used as acid alternatives in Suzuki-Miyaura coupling reactions [16], as sources to transfer phenyl groups effectively to a variety of aldehydes [17] and as COF-1 materials [18]. Boroxines are known to form stable adducts with many nitrogen donor compounds including amines [19], pyridines [20], hydrazines [21], azaindoles [22] and even salen-type ligands [23]. As compared to boroxines, arylboroxines like triphenylboroxines are finding increased utility in material science applications, such as COF-1 [19, 24], boraend functionalized polymers [25], nanoscale molecular scaffolds [26] and in generating dynamic combinatorial libraries [27].

During the last decade, great efforts were focused on the development of novel electroluminescent materials with intense luminescent efficiency, high thermal and optical stability, good charge carrier injection and

**Electronic supplementary material** The online version of this article (doi:10.1007/s12648-017-1075-2) contains supplementary material, which is available to authorized users.

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transport and desirable film morphology, as well as on the fabrication of high-performance OLED devices [28-30]. However, the electron transport properties of these materials remain challenging, particularly in terms of stability and efficiency. It is thus, important to develop high-performance electron transport materials with good stability. Maintaining efficient carrier injection in the light-emitting device is considered to be an important factor for achieving high performance devices. It is therefore, essential to synthesise light-emitting materials with a suitable energy of the highest occupied molecular orbitals (HOMO) to facilitate both hole/electron injection and transport. Alq3 [three 8-hydroxvquinolato (q) ligands chelate to the Al(III) ion in an octahedral environment] is well-known electron transport material employed both as electron transport and lightemitting material in OLEDs. According to computational calculations done by Lin et al. [31] reorganisation energy values for Alq3 were found smaller in case of hole transport (0.242 eV) as compared to electron transport (0.276 eV), which suggests it as better hole transport material. These results apparently contradict the experimental observations, which defines the role of electronic coupling factor  $(H_{da})$  in addition to reorganisation energy for charge transport in a system. However, the calculations carried out by Yang et al. [32] indicates that the electron can hop from one band to another much easier than the hole, thus implying the larger mobility for the electron than for the hole.

In molecular organic materials the conductivity studies are carried out by employing either the band like regime [33] or the hopping regime [34]. In the band like regime, transport of charge is an activation-less process occurring through bands formed by the overlapping MOs between neighbouring molecules. However, in the hopping regime the carriers are localised on one molecule through the formation of a self-trapped state and transport occurs through thermally activated hopping mechanism. According to semi-classical electron-transfer theory (Marcus electron-transfer theory) the rate of hole or electron-transfer ( $k_{et}$ ) (by hopping) is given by following equation [35, 36]

$$\boldsymbol{k}_{et} = \left(\frac{4\pi^2}{\hbar}\right) \Delta \mathbf{H}_{ab}^2 \left(4\pi\lambda_{+/-}\mathbf{T}\right)^{-\frac{1}{2}} \exp\left(\frac{-\lambda_{+/-}}{4kT}\right) \qquad (1)$$

were  $\lambda$  is reorganization energy defined as energy dissipated when a system undergone vertical electron transfer relaxes to the equilibrium geometry for its new charge distribution and  $\Delta H_{ab}$  is charge-transfer integral. From last decade several theoretical investigations on charge transport properties for OLED materials confirm that both the reorganization energies and charge transfer integrals play an important role in the electron/hole transport process

[29, 37–40] and can be evaluated by Quantum chemistry calculation.

The study of photophysical properties of TB in terms of polarizability and hyperpolarizability may define their possible role in the design and development of materials exhibiting large second-order nonlinear optical properties (NLO). However, they have not been considered until recently [41] in the context of a nonlinearity-transparency trade-off. Nonlinear optical phenomena has been an important subject of discussion over the last decades; molecules exhibiting large scale hyperpolarizabilities have a strong NLO potential and could be used, under certain conditions, for optoelectronics applications in a variety of optical devices [42-44]. Charge transfer dipolar molecules [45] and octupolar molecules [46] are well known types of systems bearing a significant NLO activity. In early 1990s, Zyss introduced the concept of octupolar molecule, with 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [47] as typical example, which is characterized by a non-dipolar and non-centrosymmetric planar C33h or D3h molecular symmetry. This invites the attention of researchers to focus on NLO active octupolar molecules, including the extension from planar two dimensional systems, like trisubstituted benzenes (triphenylbenzenes), hexasubstituted benzenes (tricyanobenzenes, trinitrobenzenes, trimethoxybenzenes, triphenyl borazine derivatives and phenylacetylenemesitylenes) and 1,3,5-triazines, to D2, D3, or Td characterized three-dimensional ones [14, 45-52]. An advantage of octupolar molecules is that they seem likely to crystallize in noncentrosymmetric space groups due to the lack of ground state dipole moment. Thus, octupolar framework provides an interesting route towards enhanced NLO responses and improved transparency.

In the present work, we have adopted quantum chemical calculations to analyze substituted **TB** derivatives,



Scheme 1 Sketch of Triphenylboroxine (TB) derivatives study using DFT at CAM-B3LYP/6-311G++ (2d, 2p) level of theory

(Scheme 1) at electronic structure level for their potential character as electron transport materials. The choice of substituents has been made in such a way that they range from strong electron releasing groups  $(-(CH_3)_2N)$  to strong electron withdrawing ones  $(-NO_2)$ . In second section, the work is intended for the optimization of the molecular structure-NLO properties relationships of **TB** with conventional electron donor or acceptor substituent groups on the phenyl ring.

The average linear polarizability  $\langle \alpha \rangle$ , first order hyperpolarizability  $\langle \beta \rangle$  and second order hyperpolarizability  $\langle \gamma \rangle$ values have been calculated from Gaussian output file using the following relations:

The microscopic polarizability (P) induced in an isolated molecule under the applied electric field (E) of an incident electromagnetic wave can be expressed by the following equation:

$$\boldsymbol{P} = \boldsymbol{\alpha}\boldsymbol{E} + \boldsymbol{\beta}\boldsymbol{E} \tag{2}$$

where P and E are related to the tensor quantities  $\alpha$  and  $\beta$  which are referred to as the polarizability and hyperpolarizability, respectively.

The definition for the polarizability [14, 38, 39] is

$$\langle \boldsymbol{\alpha} \rangle = \frac{1}{3} \big( \boldsymbol{\alpha}_{xx} + \boldsymbol{\alpha}_{yy} + \boldsymbol{\alpha}_{zz} \big)$$
(3)

the anisotropy of polarizability is

$$\Delta \boldsymbol{\alpha} = \frac{1}{\sqrt{2}} \Big[ (\boldsymbol{\alpha}_{xx} - \boldsymbol{\alpha}_{yy})^2 + (\boldsymbol{\alpha}_{yy} - \boldsymbol{\alpha}_{zz})^2 + (\boldsymbol{\alpha}_{zz} - \boldsymbol{\alpha}_{xx})^2 \\ + 6\boldsymbol{\alpha}_{xz}^2 + 6\boldsymbol{\alpha}_{xy}^2 + 6\boldsymbol{\alpha}_{yz}^2 \Big]^{1/2}$$
(4)

and the first hyperpolarizability is a third rank tensor that can be described by a  $3 \times 3 \times 3$  matrix. The components of  $\beta$  can be calculated using the following equation

$$\langle \boldsymbol{\beta} \rangle = \left[ \left( \boldsymbol{\beta}_{\boldsymbol{x}\boldsymbol{x}\boldsymbol{x}} + \boldsymbol{\beta}_{\boldsymbol{x}\boldsymbol{y}\boldsymbol{y}} + \boldsymbol{\beta}_{\boldsymbol{x}\boldsymbol{z}\boldsymbol{z}} \right)^2 + \left( \boldsymbol{\beta}_{\boldsymbol{y}\boldsymbol{y}\boldsymbol{y}} + \boldsymbol{\beta}_{\boldsymbol{y}\boldsymbol{z}\boldsymbol{z}} + \boldsymbol{\beta}_{\boldsymbol{y}\boldsymbol{x}\boldsymbol{x}} \right)^2 + \left( \boldsymbol{\beta}_{\boldsymbol{z}\boldsymbol{z}\boldsymbol{z}} + \boldsymbol{\beta}_{\boldsymbol{z}\boldsymbol{x}\boldsymbol{x}} + \boldsymbol{\beta}_{\boldsymbol{x}\boldsymbol{y}\boldsymbol{y}} \right)^2 \right]^{1/2}$$
(5)

The main objective of this study is to investigate the substitution effect in the **TB** derivatives and its influence on their energy levels, nonlinear optics and electron-transport properties. For this purposes we have investigated the molecular geometries, HOMO and LUMO levels, ionization potential, electron affinity, reorganization energy, and molecular orbitals shapes of the **TB** derivatives.

### 2. Computational Method

All geometry optimisations were performed on isolated entities in gaseous phase by employing CAM-B3LYP functional using 6-311G++ (2d, 2p) basis set at density functional level of theory [53, 54]. Structures of all derivatives completely optimized with the subsequent vibrational analysis, corresponded to a minimum on a potential energy surface (PES). The neutral molecules were treated as closed-shell systems, while for the radical anion open-shell system optimizations were carried out using a spin unrestricted wave function. Vertical electronic excitation energies were computed by using the time-dependent density functional theory (TD-DFT) [55]. The TDDFT/ CAM-B3LYP level of theory has been found quite efficient for performing significantly single-excitation calculations for the low-lying valence excited states of both closed shell and open-shell molecules [14, 40, 43]. The calculation for the lowest transitions was derived from the Gaussian output file using the GaussSum 2.2 program [56]. All the calculations were performed using the Gaussian 09 computational package [57].

#### 3. Result and Discussion

First-principle quantum chemistry calculations were performed to investigate the charge transport properties and nonlinear response of TB monomers with donor (1-6) and acceptor (8-13) substituents as shown in Scheme 1. In TB-7 the hydrogen atom on terminal phenyl rings were substituted with groups covering possibly wide range of the Hammett parameter ( $\sigma$ ) [58]. The substituent were varied from strong electron releasing groups to strong electron withdrawing ones in order to tune the electron density on central hetero-atomic ring. In first section the electronic properties of TB derivatives were studied and correlated with  $\sigma$  and structural parameters of optimised geometries. The neutral, cation and anion geometries of all the TB derivatives were optimized and the change in geometrical parameters, were obtained respectively. The optimized geometrical structures of the studied systems 1-13 are shown in Figure S1 (see supporting information). The TB-7 is composed of three phenyl rings bonded to a central six membered ring. The central ring is formed of alternative boron and oxygen atoms. The gas phase optimizations displays that terminal phenyl rings are in same plane as that of central ring. All the three B-C bonds (B<sub>3</sub>-C<sub>18</sub>, B<sub>1</sub>-C<sub>7</sub> and  $B_2$ - $C_{29}$ ), in case of **TB-7** were found of same length. To account for the substitution effect on structural parameters of TB, we carried a comparative study of change in bond lengths (B<sub>3</sub>-C<sub>18</sub>, B<sub>3</sub>-O<sub>4</sub> and X-C<sub>22</sub>) and bond angles (O<sub>5</sub>-B<sub>3</sub>-O<sub>4</sub> and C<sub>18</sub>-B<sub>3</sub>-O<sub>4</sub>). From the Table 1, we have observed that in case of neutral geometries, B<sub>3</sub>-C<sub>18</sub> bond shorten with electron donating substituent and lengthened with electron withdrawing substituents in case of TB-8, 11, 12 and 13 as compared to unsubstituted **TB-7**, while as  $B_3-O_4$  bond length elongate

ТВ	C <sub>18</sub> –B <sub>3</sub>		С <sub>22</sub> –Х		B <sub>3</sub> -O <sub>4</sub>		<o<sub>5-B<sub>3</sub>-O<sub>4</sub></o<sub>	
	NN	AA	NN	AA	NN	AA	NN	AA
1	1.54897	1.55102	1.38249	1.38519	1.38487	1.38487	118.465	118.456
2	1.54891	1.55107	1.38813	1.39452	1.38488	1.38488	118.477	118.467
3	1.54226	1.54736	1.35969	1.38007	1.38401	1.38402	118.550	118.543
4	1.54325	1.54761	1.36209	1.38064	1.38403	1.38403	118.543	118.536
5	1.54580	1.54864	1.51205	1.52536	1.38299	1.38299	118.561	118.552
6	1.54547	1.54832	1.50881	1.52510	1.38334	1.38334	118.540	118.532
7	1.55102	1.55640	1.08468	1.11032	1.38280	1.38280	118.577	118.571
8	1.55378	1.55858	1.34910	1.37121	1.38271	1.38271	118.636	118.630
9	1.55032	1.55278	1.75767	1.76547	1.38243	1.38243	118.617	118.608
10	1.54830	1.55278	1.91619	1.93806	1.38236	1.38236	118.610	118.603
11	1.55378	1.55936	1.49024	1.51660	1.38185	1.38185	118.651	118.645
12	1.55489	1.56096	1.43122	1.45839	1.38160	1.38160	118.680	118.674
13	1.55767	1.56568	1.48476	1.52359	1.38084	1.38084	118.702	118.699

Table 1 Some bond lengths and bond angle of Triphenylboroxine (TB) derivatives in neutral and anionic states calculated at CAM-B3LYP/6-311G++ (2d, 2p) level

with electron donating substituent and shorten with electron withdrawing groups. The contraction of  $B_3$ - $C_{18}$  bond in case 1, 2, 3, 4, 5 and 6 in substituted TBs results from enhanced electron density due to electron donating groups on the phenyl ring, which results in effective back bonding to adjacent boron atom. The elongation of B<sub>3</sub>-C<sub>18</sub> bond in case of 8, 11, 12 and 13 is due to scarcity of electron density caused by electron withdrawing groups, which result in more effective attraction of oxygen on electron deficient boron atom, as also reflected from contraction of B<sub>3</sub>-O<sub>4</sub> bond. However, the C<sub>22</sub>-X elongates both in case of electron releasing or electron withdrawing substituents as compared to the parent TB-7. In all the neutral optimised geometries the planarity of phenyl rings around boron atom is maintained and has been quantified in terms of key BLA (Bond length Alternation) values of **TB** derivatives. In this work, we have calculated a local BLA associated with B<sub>3</sub>- $C_{18}$ ,  $C_{18}=C_{20}$  and  $C_{20}=C_{23}$  bond lengths according to the definition framed by Fu et al. [59] given by Eq. 6;

$$\mathbf{BLA} = \frac{\mathbf{d}(\mathbf{B}_3 - \mathbf{C}_{18}) + \mathbf{d}(\mathbf{C}_{20} - \mathbf{C}_{23})}{2} - \mathbf{d}(\mathbf{C}_{18} = \mathbf{C}_{20})$$
(6)

Upon substitution by denoting groups it was observed that **TB** derivatives shows an increased double bond character of the central single bond, indicating the degree of conjugation increasing as compared to **TB** derivatives with electron withdrawing substituents. The electron density increase due to electron donating groups on **TB-7** in the order of 7 < 6 < 5 < 4 < 3 < 2 < 1 and the BLA values increases from 0.201 (1) < 0.209 (2) < 0.227 (3) < 0.311 (4) < 0.319 (5) < 0.331 (6) < 0.333 (7). This trend indicates that the degree of conjugation is increasing

upon the substitution with electron donating groups. In case of TB derivatives with halogen groups i.e. in 8, 9 and 10 electron withdrawing capacity decreases the as 8 > 9 > 10, whereas the BLA values do not differ much in TB-8 and TB-9 (0.390 (8) < 0.391(9), and the TB-10 opts maximum BLA value (0.429). The TB-13 and TB-12 have maximum electron withdrawing capacity, with BLA values 0.411 and 0.407 respectively. In order to understand the effect of charge injection into TB systems, we optimized the anionic geometry (i.e., the neutral molecule in the presence of an extra electron) and calculated change in geometrical parameters and electron releasing power of these molecules. The calculation reveals change in geometrical parameters of studied molecules from changing neutral to radical-anion geometry (see Table 1). In case of **TB-7**, the bond lengths  $C_{18}$ - $B_3$ ,  $C_{22}$ -X and  $B_3$ -C<sub>4</sub> change from 1.551 to 1.084, 1.382 to 1.556 and 1.110 to 1.398 Å respectively. However, the internal angles of central heterocyclic ring show insignificant change. Similar trend was observed for all the derivatives. From Table 1, it was found, that the amplitude of the structural along modifications increase moving from electron donating substituents to electron withdrawing substituents. It is worth mentioning that the substitution ranging from diamethylamino group to nitro group for hydrogen i.e. group with lowest Hammett value to group with highest Hammett value, affects the C-B bond lengths and <B-O-B bond angle, which indicates the existence of strong correlation between  $\sigma$  and the geometrical parameters, as is evident from the Figure S2a and S2b (supporting information). The changes in geometrical parameters on substitution are attributed to lowering of energy due to back bonding, the increase in electron

density on boron by electron donating groups and the increase in energy caused by contraction of B–O bond in case of **TB** derivatives containing electron withdrawing groups. The contraction of  $C_{18}$ –B<sub>3</sub> bond length in the substituted **TBs** in neutral states on the substitution by electron donating groups as compared to electron withdrawing groups and reverse in case of the anionic states indicates an effect of conjugation and  $\pi$ -electron delocalization. The optimized anionic geometries do not show much structural changes as compared to the neutral molecules, which imply lesser reorganisation of molecular framework on the injection of one negative charge. This property of the **TB** systems allows tuning their electron transport property in OLED.

We calculated the ionisation potential (IP), vertical electron affinity (VEA), adiabatic electron affinity (AEA), and reorganization energy for electron transport using the Scheme-S1 (see supporting information) and the results are in Table 2. For an electron material to be efficient, the electron affinity is expected to be high enough to ensure that the electrons come across the energy barrier and allow efficient injection of the electrons into the empty LUMO of the semiconductor molecules [6, 31, 33]. From Table 2, it is clear that the value of  $\lambda_{e}$  decrease for **TB** derivatives with electron releasing (1-6) and slightly increase for electron withdrawing (8-13) substituents as compared to unsubstituted **TB-7**. The effect on  $\lambda_e$  is much more prominent in case of electron withdrawing substituents, as compared to electron donating substituents. The low  $\lambda_e$  in case of **TB** derivatives **1–6** is expected to display a significant charge transport as compared to TB-7. In case of derivatives with electron withdrawing group the  $\lambda_e$  for **TB** 

**Table 2** Vertical electron affinity (VEA), adiabatic electron affinity (AEA), reorganization energy ( $\lambda_e$ ) for electron transport (eV) calculated by using DFT at CAM-B3LYP/6-311G++ (2d, 2p) level of theory and Hammett value ( $\sigma$ ) of **TB** derivatives

ТВ	VEA (eV)	AEA (eV)	$\lambda_1$	$\lambda_2$	$\lambda_{e}$	σ
1	1.020	0.913	0.044	0.107	0.108	-0.83
2	0.997	0.880	0.035	0.116	0.118	-0.66
3	0.775	0.619	0.079	0.155	0.158	-0.37
4	0.755	0.598	0.070	0.158	0.160	-0.268
5	0.506	0.350	0.090	0.157	0.160	-0.17
6	0.554	0.393	0.073	0.161	0.164	-0.15
7	0.455	0.292	0.039	0.163	0.165	0
8	0.302	0.140	0.072	0.162	0.164	0.062
9	-0.054	-0.215	0.084	0.161	0.164	0.22
10	-0.077	-0.238	0.103	0.161	0.164	0.232
11	-0.650	-0.815	0.097	0.165	0.169	0.45
12	-0.953	-1.118	0.124	0.166	0.170	0.66
13	-1.509	-1.707	0.140	0.198	0.203	0.778

derivative with halogen substituents (8, 9 and 10) is same and is equal to the  $\lambda_e$  of methyl derivative. The remaining TB derivatives with electron withdrawing groups follow the trend:  $-COOH < -CN < -NO_2$ . For the **TB**s with the electron releasing group, the reorganization energies values follows order:  $-CH_3 > -C_2H_5 = -OH > -OCH_3 > -NH_2 >$ -N(CH<sub>3</sub>)<sub>2</sub>. We developed the correlation for defining parameters that influence the  $\lambda_e$  in terms of the geometry change upon injection of one negative charge. The Fig. 1a, b show correlation of  $\lambda_e$  with  $\sigma$ . In case of electron withdrawing groups the trend is irregular; halogen derivatives shows different geometrical changes, while the reorganization energies are same. Strong electron donating substituents  $(-NH_2 \text{ and } -N(CH_3)_2)$  cause the **TB** derivatives to undergo lesser geometry changes compared to other electron donating substituents which is also reflected from their lowest value of  $\lambda_{e}$  among all the derivatives. In addition to



Fig. 1 Plot of reorganization energy with Hammett parameter (a) derivatives with electron releasing groups and (b) derivatives with withdrawing groups

ТВ	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	$\Delta E_{(HOMO-LUMO)}$	<sup>a</sup> ΔHOMO	<sup>b</sup> ΔLUMO	Ip (eV)
1	-5.179	-2.573	2.606	1.536	0.976	6.202
2	-5.574	-2.706	2.868	1.141	0.843	6.726
3	-5.934	-3.171	2.762	0.781	0.378	7.255
4	-6.277	-3.353	2.924	0.438	0.196	7.477
5	-6.425	-3.424	3.001	0.290	0.125	7.830
6	-6.466	-3.424	3.043	0.370	0.125	7.862
7	-6.715	-3.549	3.166	_	_	8.367
8	-6.836	-3.645	3.192	0.121	-0.096	8.316
9	-7.091	-3.891	3.200	-0.376	-0.341	8.272
10	-7.202	-3.925	3.277	-0.487	-0.376	8.113
11	-7.342	-4.002	3.340	-0.627	-0.453	8.644
12	-7.811	-4.084	3.727	-1.096	-0.534	8.950
13	-8.432	-4.475	3.957	-1.717	-0.925	9.305

Table 3 Calculated HOMO, LUMO energies, ionisation potentials (Ip) of studied TB derivative calculated at CAM-B3LYP/6-311G++ (2d, 2p) level of theory

<sup>a</sup>  $\Delta$ (HOMO) = E<sub>(HOMO TB derivative)</sub> - E(HOMO<sub>TB</sub>)

<sup>b</sup>  $\Delta$ (LUMO) = E<sub>(LUMO TB derivative)</sub> - E(HOMO<sub>TB</sub>)

 $\lambda_e$  the electron affinity of derivatives is another factor which governs the rate of electron addition or extraction. We calculated vertical and adiabatic electron affinities at CAM-B3LYP/6-311G++ (2d, 2p) level of theory and the results are shown in Table 2. From Table 2, we observed that the vertical electron affinity for TB derivatives with electron donating substituent have positive value, whereas the derivatives with electron withdrawing groups except floro derivative (8) have negative electron affinity. This reflects the enhanced electron transport efficiency of TB derivatives (1-6) as compared to TB-7. In addition to it, EAs calculated for the derivatives **1–6** are higher than the values reported for the molecular oxygen [60]. So, these compounds in anionic form seem to be quite stable towards quenching caused by molecular oxygen present in the atmosphere.

To characterize the electronic and optical properties of molecular systems it is useful to examine energies of levels (bands) allowed for electrons and holes, energy gap  $(\Delta E_{LUMO-HOMO})$  between these bands and the distribution patterns of the Frontier molecular orbitals (FMO). The  $\Delta E_{LUMO-HOMO}$  is the differences of energy of lowest unoccupied molecular orbital (E<sub>LUMO</sub>) and energy of highest occupied molecular orbital (E<sub>HOMO</sub>), allowed for non-interacting electrons and holes. The energies of the HOMO and LUMO levels used for the calculation of the energy gap were calculated using DFT, employing CAM-B3LYP/6-311G++ (2d, 2p) level performed for isolated molecules (see Table 3). We observe from Table 3 that HOMO level of TB derivatives increase with electron donating substituents and apparently decreases with electron withdrawing substitutes. This behaviour is explained in terms of enhanced  $\pi$ -conjugation due to electron-releasing environment created by electron rich substituents resulting in increased electron density on central Boron atoms. The HOMO energies are in the order of 1 > 2 > 3 > 4 > 5 > 6 > 7 and their energy gap increases in the order of 1 < 2 < 3 < 4 < 5 < 6 < 7. These results reveal that the TB-1 and TB-2 derivatives possess narrower energy gap values due to their better conjugation resulting from enhanced electron density on account of electron rich substituent. The calculated IP and EA values for TB derivatives were not correlated with experimental values as the data was not available in literature, however computationally calculated values of IP and EA correlated quite well with  $\sigma$  of studied systems (see Fig. 2a, b). The FMO (Fig. 3) studies reveals that the HOMOs of the neutral molecules delocalize over the three phenyl rings including bridging oxygens atom of central ring. The LUMOs have an obvious electron density distribution over two phenyl rings including boron atom and substituents, with a small contribution from oxygen atom present in central ring. Thus, the charge transfer orientation is associated with the difference between the HOMO of the donor (phenyl rings) and LUMO of the acceptor (boron atoms), which is an imperative factor to effect charge ejection efficiency. However in case of TB-13, the HOMO is primary located on two phenyl rings and LUMO is delocalized over whole skeleton of the derivatives. We observe that, there are antibonding in the single bonds and bonding in the double bonds in the HOMOs of TBs (1-12). On the contrary, there are bonding in the single bonds and antibonding in the double bonds in TB-13, possible reason is presence of strong electron withdrawing groups in TB-13. In order to



**Fig. 2** Plot of Hammett Parameter with (a) electron affinity (eV) and (b) ionization potential (eV) for the series of studied **TB** derivates

understand the effect of substituents on the electronic transition associated with **TB** derivatives TD-DFT calculation were carried in vacuum at CAM-B3LYP level of theory. We have observed that  $\Delta E_{LUMO-HOMO}$  are reduced under the effect of inserting electron donating groups, introducing a red shift in corresponding absorption band, with maximum shift in case of **TB-1** with dimethylamine as substituent. The maximum absorption band corresponds to the electronic transition occurring mainly from HOMOs including phenyl rings to the LUMOs including Boron atoms.

For organic molecules containing an electron donor (D) and acceptor (A) and linked through a  $\pi$ -conjugated bridge, the consummation of the quantum chemistry computation methods provide the powerful approach to pursue their nonlinear response. We can quantify the nonlinear properties in term of theoretically calculated

polarizability and the hyperpolarizability ( $\beta$ ) of organic system. First hyperpolarizability which contributes to the second order behaviour, may be related using a simple powerful relationship [42] to the dipole change between the ground and excited state. The first hyperpolarizability is a strong function of the absorption maximum especially in dipolar systems [61], so the high  $\beta$  values are generally accompanied by absorption at large wavelengths. According to Oudar and chelma,  $\beta$  is related to low-lying charge-transfer transition through a two level model [61] on the basis of the complex sum over states (SOS) expression as;

$$\boldsymbol{\beta} \propto \left(\boldsymbol{\mu}_{ee} - \boldsymbol{\mu}_{gg}\right) \frac{\boldsymbol{\mu}_{ge}^2}{\boldsymbol{E}_{ge}^2} \tag{7}$$

where  $(\mu_{ee} - \mu_{gg})$  is the difference between the dipole moments of the *m*th excited state and ground state respectively,  $\mu_{ge}$  is the transition dipole, and  $E_{ge}$  is the transition energy.

According to two-level model, materials with wellperforming NLO property should possess a low lying charge transfer excited states with good oscillator strength [61, 62]. The calculated values for  $\beta$  at DFT/CAM-B3LYP/6-311G++ (2d, 2p) and for  $E_{ge}(excitation$ energy) at TD-DFT/CAM-B3LYP/6-311G++ (2d, 2p) level of theory are given in the Table 4. We have observed that the **TB** derivatives from 1 to 6 displays higher  $\beta$  values as compared to **TB-7**. In case of **TB** derivatives with electron releasing groups, the  $\mu_{ge}^2/E_{ge}^2$ decrease in the order 1 > 2 > 4 > 3 > 6 > 5 and the trend is in accordance with the  $\beta$  values, except in case of methyl and ethyl derivatives, the methyl derivatives have lower values of  $\mu_{ge}^2/E_{ge}^2$  but higher value of  $\beta$  as compared to ethyl derivative. TB derivatives with electron withdrawing substituents (8–13) displays higher value for  $\beta$ and lower value for  $\mu_{ge}^2/E_{ge}^2$  as compared to **TB-7**. Among TB derivatives 8-13 the nitro derivative show highest value of  $\mu_{ge}^2/E_{ge}^2$  with maximum  $\beta$ . Thus, the contribution of the square form to the two level model dominates the major effect to the  $\beta$ . If we compare the two extreme derivatives in the series i.e. nitro (strongest electron withdrawing group) and dimethylamine (strong electron donating group), the values of  $\beta$  are completely according to two model equation and depends upon the transition dipole and transition energy of a group. The  $\mu_{ge}^2/E_{ge}^2$  TB-7 is close to that of **TB-13**, whereas the  $\beta$  of latter is 4 times as compare to the former. Thus, the value of  $\beta$  is also effected by other parameters like size and electronegativity of substituents.

The energy levels studies revealed that in case of studied **TB** system as the hydrogen atom is replaced by the dimethylamine group the HOMO energy level rises



Fig. 3 The frontier molecular orbitals (FMOs) of TB derivatives at DFT/CAM-B3LYP/6-311G++ (2d, 2p) level of theory

resulting reduction in energy gap. Thus, the electron density of the HOMO orbital of **TB-1** derivative would favour the charge transfer to the LUMO orbital, on account of reduction in  $\Delta E_{LUMO-HOMO}$ . Similarly, on comparing the

**TB** derivates **3** and **4** with **TB-7**, we have observed that both the HOMO and LUMO levels changes, favouring the higher  $\beta$  value for the former derivatives than later. Thus, on account of these observation we may conclude that **TB** 



Fig. 3 continued

derivative with low energy gap corresponds to lower first transition energy is an important measure of the  $\beta$  in case of such molecules. However, in case of **TB** derivatives with electron withdrawing groups, the **TB** derivative with highest  $\Delta E_{LUMO-HOMO}$  have maximum value of hyperpolarizabilities. The reason of this effect is that the first excitation includes only 12% contribution from the HOMO to LUMO population along with other transitions.

On studying the effect of geometrical parameters on the value of  $\beta$  of **TB** derivatives, no clear dependence is observed in case of **TB** molecules with the electron donating groups. The B<sub>3</sub>-C<sub>18</sub> bond length is observed to be minimum for methoxy derivative and maximum for dimethylamine derivative and follows the order 3 < 4 < 6 < 5 < 2 < 1 same trend followed by  $\beta$ . However, the B<sub>3</sub>-O<sub>4</sub> bond length follows the trend

TB	$\lambda_{\text{max}}$	Major contribution	f	$E_{ge}\left( eV\right)$	$\mu_{ge}^2$	$\mu_{ge}^2/E_{ge}^2$	$\substack{\beta_{total} \\ (\times 10^{-30} \text{ esu})}$
1	294.34	HOMO- > LUMO (94%)	0.4116	4.134	0.469	0.0274169	1754.233
2	290.62	HOMO- > LUMO (87%)	0.1948	4.266	0.435	0.0238784	1350.165
3	277.52	HOMO- > LUMO (71%)	0.3278	4.468	0.366	0.0183199	843.6561
4	263.99	HOMO- > LUMO (89%)	0.1575	4.766	0.443	0.0194972	1003.662
5	263.69	HOMO- > LUMO (80%)	0.3403	4.779	0.095	0.0041686	841.6085
6	263.35	HOMO- > LUMO (79%)	0.2652	4.782	0.126	0.0054954	529.6651
7	260.15	HOMO- > LUMO (89%)	0.1575	4.794	0.087	0.0037839	152.5521
8	262.77	HOMO- > LUMO (52%)	0.078	4.774	0.062	0.0027403	202.0045
9	259.15	HOMO- > LUMO (88%)	0.2551	4.835	0.042	0.0017879	283.0655
10	256.44	HOMO- > LUMO (92%)	0.3823	4.987	0.041	0.0016663	300.7245
1	249.03	HOMO- > LUMO (92%)	0.0046	5.087	0.019	0.0007212	383.6084
12	248.53	HOMO- > LUMO (43%)	0.1633	5.097	0.014	0.0005266	445.7342
13	246.32	H-2- > L+1 (22%), H-1- > L+1 (21%), HOMO- > LUMO (12%)	0.0172	5.133	0.102	0.0038708	512.0743

Table 4 Results of TDDFT calculations at CAM-B3LYP/6-311G++ (2d, 2p) level of theory for the electron transitions of TB systems

3 < 4 < 6 < 5 < 1 < 2 and  $\beta$  decreases as 1 > 2 > 4 > 3> 5 > 6. In addition to geometrical parameters we also correlated the  $\beta$  values with  $\sigma$  of **TB** derivatives. The plots of the  $\beta$  of **TB** derivatives as a function of  $\sigma$  in Fig. 4a, b displays inverse and direct relation in case of electron donating and electron withdrawing groups respectively.

As earlier mentioned, changing the donor group from dimethylamino to methyl group effects the  $B_3-C_{18}$ ,  $C_{18}=C_{20}$  and  $C_{20}-C_{23}$  bond lengths. In case of TB derivatives from 1 to 6 (strong electron donating groups) the  $B_3$ - $C_{18}$  shortens and  $C_{18}$ = $C_{20}$  lengthened. In this situation BLA (bond length Alternation) values were calculated by using Fu et al. equation related to  $B_3-C_{18}$ ,  $C_{18}=C_{20}$ and C<sub>20</sub>-C<sub>23</sub> bonds. In case of TB derivatives with electron donating groups, the  $\beta$  decrease as; 1754.23  $\times$  10<sup>-30</sup> esu (1) >  $1350.16 \times 10^{-30}$  esu (2) >  $1003.66 \times 10^{-30}$  esu (4) >  $843.65 \times 10^{-30}$  esu (3) >  $841.60 \times 10^{-30}$  esu (5) > 529.66 (6)  $\times 10^{-30}$  esu > 152.55 (7)  $\times 10^{-30}$  esu and the BLA value increases as 0.201 (1) < 0.209(2) < 0.227(4) < 0.319 (5) < 0.331**(3)** < 0.311 (6) < 0.333 (7). This reflects that increase in the strength of donor groups from methyl to dimethylamine have a pronounced impact on the hyperpolarizabilities. In case of the **TB** derivatives containing halogen substituent  $\beta$  increases with increases in BLA values. The TB derivatives with carboxy and cyano groups, the BLA does not change but the former have lower  $\beta$  value than later. However, **TB-13** opts maximum value for BLA and  $\beta$  among the **TB** derivatives containing electron withdrawing groups. This indicates that the in case TB derivatives with electron withdrawing groups BLA values shows irregular dependence on the  $\beta$  values. Thus, from these calculation, we may conclude that electron donating substituent will increase the nonlinear response of **TB** systems.

#### 4. Conclusion

Systematic DFT calculations were carried out on a series of **TB** derivatives. The geometrical parameters of optimized **TB-7** at CAM-B3LYP/6-311G++ (2d, 2p) level are in good agreement with the experimental result. It is evident from the calculations that the  $B_3-C_{18}$  bond length shorten with electron donating substituent and elongates with electron withdrawing substituents as compared to unsubstituted TB-7, while B<sub>3</sub>-O<sub>4</sub> bond lengths elongate with electron donating substituent and shorten with electron withdrawing groups. However, the C<sub>22</sub>-X bond elongates both in case of electron releasing or electron withdrawing substituents as compared to the parent TB-7. The electron density in TB derivatives increase order in 6 < 5 < 4 < 3 < 2 < 1 and calculated local BLA values increases from 0.201 (1) < 0.209 (2) < 0.227 (3) < 0.311(4) < 0.319 (5) < 0.331 (6) < 0.333 (7), indicating that the degree of conjugation is increasing upon the substitution with electron donating groups. The change in geometrical parameters on substitution are attributed to lowering in energy due to back bonding, increasing electron density on boron by electron donating groups and increase in energy caused by contraction of B-O bond in case of TB derivatives with electron withdrawing groups. For the TB derivatives with electron donating groups (1-6)  $\lambda_{e}$ decreases and slightly increase for electron withdrawing (8-13) substituents as compared to unsubstituted TB-7.



Fig. 4 Plot of Hammett Parameter with hyperpolarizability of (a) TB derivative with electron releasing group and (b) TB derivates with electron withdrawing groups

The electron donating substituents increases the HOMO level of **TB**, while as there is apparent decrease in the HOMO level of electron withdrawing substitutes, due to enhanced effect of  $\pi$ -conjugation in case of former. With the change in substituent from hydrogen to dimethylamino group, the static hyperpolarizability becomes larger due to increased electron density. Analysing the  $\beta$  data of **TB** derivatives makes it possible to find their potential applications in nonlinear devices.

# 5. Supporting Information

Supporting information contains Figure S1 (Optimized geometries of the series of studied Triphenylboroxine (**TB**) derivates), Figure S2 (Plot of geometrical parameters with the Hammett Parameter (a) bond length versus Hammett parameter, for

the series of studied **TB** derivates) and Scheme S1 (Calculation details of the reorganization energy for the electron transport,  $\lambda_1$  is reorganization energy of a anionicradical and  $\lambda_2$  reorganization energy of a neutral molecule).

Table S1 (Optimized geometrical parameters bond length (Å) and bond angles (deg.) of Triphenylboroxine **(TB-7)**.

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