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Bis-aryl substituted dioxaborines as electron-transport materials: a comparative density functional theory investigation with oxadiazoles and siloles

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Abstract

We report on a detailed quantum-chemical comparison of the electronic structures, vertical electron affinities, and intramolecular reorganization energies for bis-aryl substituted dioxaborine, oxadiazole, and silole derivatives. The results indicate that the HOMO and LUMO energies of the substituted compounds can be tuned on the order of 2–3 eV via minor changes in the substitution patterns, with the HOMO and LUMO levels for the dioxaborine derivatives consistently the most energy stabilized. Additionally, large vertical electron affinities and comparable intramolecular reorganization energies confirm that dioxaborine systems are interesting candidates for electron transport materials.

1. Introduction

Organic, π-conjugated materials display semiconducting properties that allow for the low-cost fabrication of new generations of thin-film electronic, optoelectronic, and electrooptic devices such as light-emitting diodes, photovoltaic cells, field-effect transistors, and photorefractive cells [1,2]. The successful implementation of such devices in commercial applications requires the design of materials with large carrier mobilities of both holes and electrons. Thus, it is of importance to consider the optimization of such physico-chemical properties as redox potentials, radical-ion stabilities, relaxation energies, and luminescence yields [3]. While hole-transport materials (e.g. triarylamine derivatives [4,5]) have been relatively ubiquitous in the development and investigation of organic-based electronic devices, electron-transport materials have only recently undergone a substantial increase in consideration and design [6–8] due to a number of difficult key issues facing their development; these include electrochemical stability of the radical-anion versus molecular oxygen and water under ambient operating conditions [3,8], and the difficulty of optimization of lowest-unoccupied molecular orbital (LUMO) energies to complement the Fermi energies of a variety of cathode materials in order to facilitate the injection of electrons [2]. Additionally, electron mobilities comparable to hole mobilities have yet to be attained [9].

Among the most effective and successful electron transport materials to date are those based upon oxadiazole [1,3,4-oxadiazole] and silole [1,1′-dimethylsilacyclopentadiene] derivatives. Several studies indicate that oxadiazole-based systems have both efficient electron-transport and hole-blocking properties in a variety of molecular architectures, including small molecule

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[10], polymer [11], and dendritic forms [12]. Silole derivatives display nondispersive and air-stable electron transport with mobilities two orders of magnitude greater than tris(8-hydroxyquinolinolato) aluminum (III) (Alq_3) [9], another widely used electron transport material. These silole derivatives also have very high solid-state photoluminescence quantum yields in the absence of dopants [13].

The photoexcited state properties of dioxaborine [2,2-difluoro-1,3,2-oxaoxoniaboratine] derivatives have undergone investigation for a wide variety of functions, including: photocycloaddition and photoinduced electron-transfer reactions [14,15] and two-photon absorption chromophores for the photodeposition of silver [16]. More recently, dioxaborines have also been envisioned as building blocks for new series of molecular electron transport materials in organic electronic devices due to their electronic (high electron affinities, reversible electrochemistry) and optical (absorption in the visible range, large fluorescence quantum yields) properties [17,18]. Recent time of flight measurements have revealed electron mobilities two orders of magnitude larger than Alq_3 for this class of materials [17].

In this paper, we report the results of a quantum-chemical assessment of bis-aryl substituted dioxaborines and their comparison to oxadiazole and silole model compounds, see Fig. 1. We use Density Functional Theory (DFT) to assess the electronic structure, vertical electron affinities, and intramolecular reorganization energies of these molecules. Our analysis also allows us to directly compare the one-particle molecular orbital properties that are commonly found in organic device literature (i.e. molecular orbital levels aligned relative to the Fermi energy of the electrodes) with (physically observable) properties such as electron affinities.

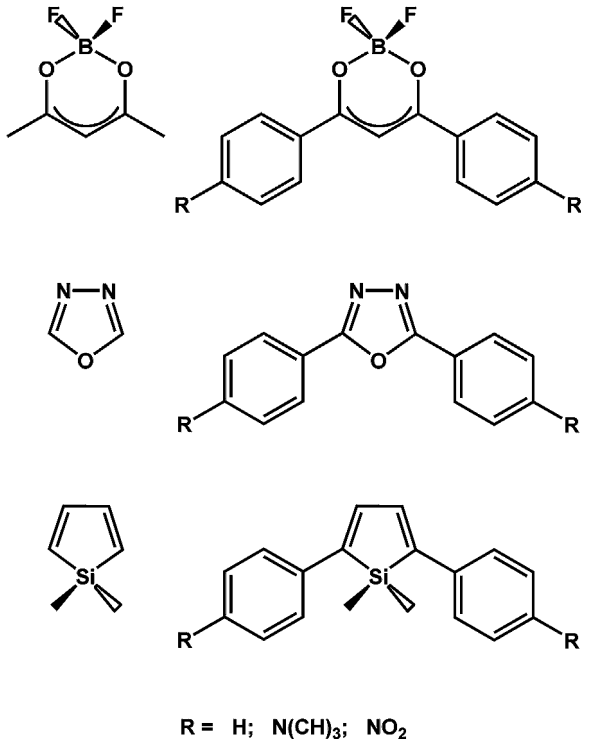

Fig. 1. Chemical structure of dioxaborine (top), oxadiazole (middle), silole (bottom), and their bis-aryl substitution patterns.

2. Theoretical methodology

The systems of interest include dioxaborine bis-aryl substituted at the 1- and 3-positions, and oxadiazole and 1,1-dimethylsilole substituted at the 2- and 5-positions; the aryl substituents are phenyl, *p*-*N*,*N*-dimethylaminophenyl, and *p*-nitrophenyl, see Fig. 1. Geometry optimizations of the neutral and radical-anion electronic configurations were performed by DFT calculations with the B3LYP functionals and a 6-31G* double-zeta plus polarization basis set. DFT methods have been proven to successfully evaluate the geometric and energetic properties of a number of small-molecule radical-anions with the incorporation of basis sets containing diffuse functions [19]. To account for the proper description of the radical-anion state and provide qualitative estimates of such properties as electron affinity, single-point calculations were carried out with a 6-31+G* basis set for each molecular structure optimized at the 6-31G* level. All DFT calculations were carried out with Gaussian 98 (Revision A.11) [20].

3. Results and discussion

In the following Section, we present a qualitative molecular orbital analysis of the chemical structures shown in Fig. 1 as a means to compare their potential hole-blocking and electron-injection properties. Section 3.2 validates this comparison based on molecular orbitals by direct calculation of the vertical electron affinities. Finally, in Section 3.3, we evaluate the intramolecular reorganization energies, which are a key component of electron transport in the hopping regime [21].

3.1. Molecular orbitals

The DFT-calculated highest-occupied π-molecular orbitals for the dioxaborine, oxadiazole, and silole rings fall within a range of 2 eV, see Table 1, with the oxadiazole molecular orbital being the most stable. The dioxaborine (−7.68 eV) highest-occupied molecular orbital (HOMO), see Fig. 2, is characterized by an allylic-like orbital pattern between the three carbon atoms contained within the ring and an antibonding pattern with

Table 1
HOMO and LUMO energies for the dioxaborine, oxadiazole, and silole compounds at the B3LYP/6-31+G*//B3LYP/6-31G* level of theory

Compound	Bis-substituent	HOMO (eV)	LUMO (eV)
Dioxaborine	Methyl	−7.68 (0.00)	−2.57 (0.00)
	N,*N*-Dimethylaminophenyl	−5.55 (+2.13)	−2.22 (+0.35)
	Phenyl	−7.04 (+0.64)	−3.04 (−0.47)
	Nitrophenyl	−7.97 (−0.29)	−4.23 (−1.66)
Oxadiazole	Hydrogen	−8.42 (0.00)[a]	−1.01 (0.00)
	N,*N*-Dimethylaminophenyl	−5.09 (+3.33)	−1.18 (−0.17)
	Phenyl	−6.44 (+1.98)	−1.96 (−0.95)
	Nitrophenyl	−7.49 (+0.93)	−3.67 (−2.66)
Silole	Hydrogen	−6.25 (0.00)	−1.47 (0.00)
	N,*N*-Dimethylaminophenyl	−4.47 (+1.78)	−1.50 (−0.03)
	Phenyl	−5.46 (+0.79)	−2.04 (−0.57)
	Nitrophenyl	−6.45 (−0.20)	−3.45 (−1.98)

For each compound, the energy difference from the reference dioxaborine, oxadiazole, or silole ring is given in parentheses.
[a] The energy of the highest π-molecular orbital is listed here due to the fact that the B3LYP/6-31+G*//B3LYP/6-31G* HOMO was of σ-nature.

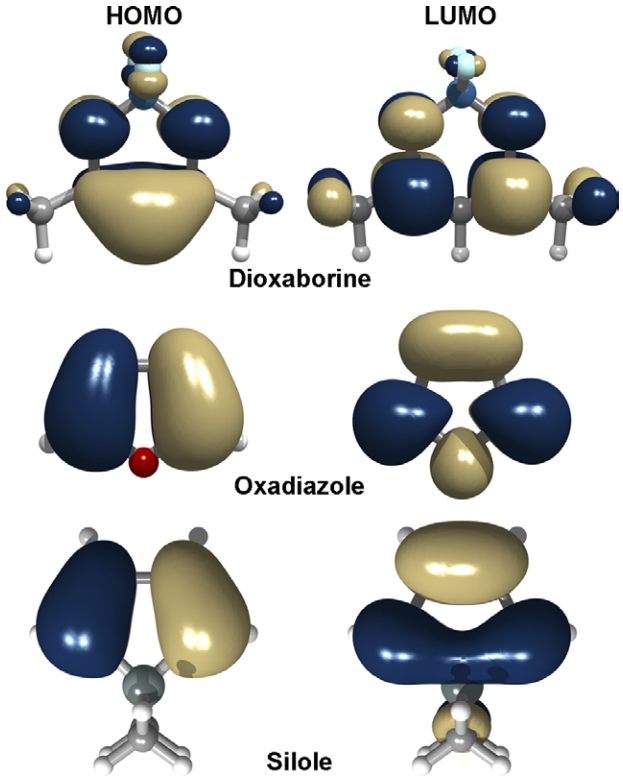

Fig. 2. B3LYP/6-31G*//B3LYP/6-31+G*-calculated highest occupied (HOMO) (left) and lowest unoccupied (LUMO) (right) molecular orbitals for dioxaborine (top), oxadiazole (middle), and silole (bottom). Note that the oxadiazole HOMO is taken as the highest π-molecular orbital.

the oxygen atoms [18]. For oxadiazole (−8.42 eV) and silole (−6.25 eV), the highest π-molecular orbitals reside on the *cis*-diazabutadiene and *cis*-butadiene moieties, respectively, the presence of the nitrogen atoms in oxadiazole pushing the orbital energy down; the bonding–antibonding pattern is consistent with butadiene structures. The lowest-unoccupied one-electron molecular orbitals (LUMOs) of the unsubstituted rings lie within a slightly smaller range of energies (∼1.5 eV). Importantly, the LUMO energy for dioxaborine lies significantly lower than the oxadiazole and silole equivalents. The dioxaborine LUMO (calculated here to be −2.57 eV) possesses the interesting feature of an allylic-like non-bonding orbital among the three carbon atoms contained within the ring. The oxadiazole LUMO (−1.01 eV) is characterized by a bonding interaction between the two nitrogen atoms and an antibonding interaction amongst all other heavy atoms. The silole LUMO (−1.47 eV) reveals the characteristic σ*–π* conjugation in the ring due to interaction between the σ*-orbitals of the two exocyclic σ-bonds on the ring silicon with the π*-orbital of the butadiene moiety that provides the stable features of the molecular orbital.

Upon bis-phenyl substitution, the HOMO energies for the substituted dioxaborine (−7.04 eV), oxadiazole (−6.44 eV), and silole (−5.46 eV) compounds are destabilized relative to the isolated rings, as expected from the increased conjugation. The HOMO wavefunctions are fully delocalized throughout each system, see Fig. 3; it is observed that each molecular orbital contains a nodal plane between the core highest molecular π-orbital and one of the molecular orbitals derived from the doubly-degenerate benzene HOMOs on the phenyl. The LUMO wavefunctions of the bis-phenyl dioxaborine (−3.04 eV), oxadiazole (−1.96 eV) and silole (−2.04 eV) are stabilized relative to the isolated rings; as with the HOMO wavefunctions, the molecular orbitals are delocalized for each system and there now exists bonding character between the core ring and the phenyl units.

The HOMOs and LUMOs of the bis-donor (*p*-*N*,*N*-dimethylaminophenyl) and bis-acceptor (*p*-nitrophenyl) substituted structures (as depicted by the representative example of the bis-substituted dioxaborine systems in Fig. 4) reveal the anticipated opposite effects [22]. Bis-aryl substitution with electron-donating *p*-*N*,*N*-dimethylaminophenyl groups destabilize the HOMO energies

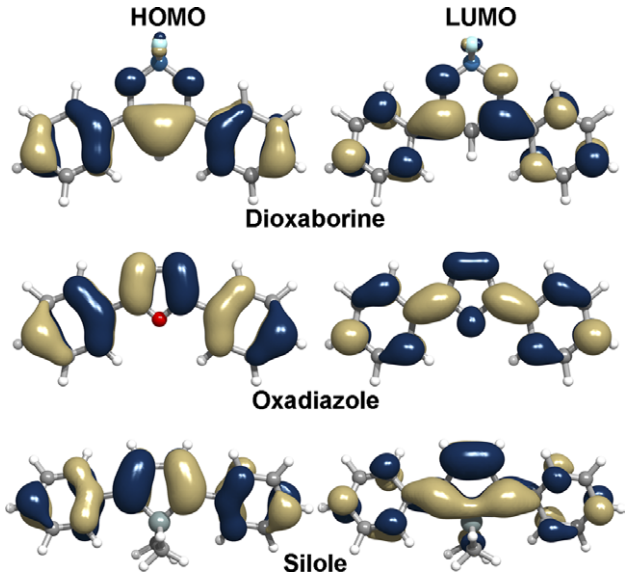

Fig. 3. B3LYP/6-31+G*//B3LYP/6-31G*-calculated highest occupied (HOMO) (left) and lowest unoccupied (LUMO) (right) molecular orbitals for bis-phenyl substituted dioxaborine (top), oxadiazole (middle), and silole (bottom).

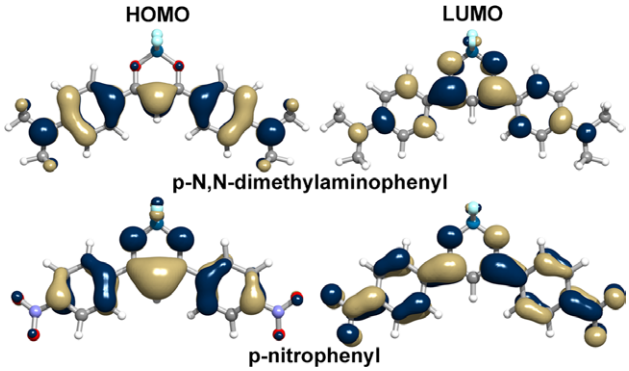

Fig. 4. B3LYP/6-31+G*//B3LYP/6-31G*-calculated highest occupied (HOMO) (left) and lowest unoccupied (LUMO) (right) molecular orbitals for bis-*p*-*N*,*N*-dimethylaminophenyl substituted (top) and bis-*p*-nitrophenyl (bottom) substituted dioxaborines.

considerably, by about 2–3 eV versus the cores, while the effect on the LUMO energies is much smaller, see Table 1. This trend is reversed for the electron-withdrawing *p*-nitrophenyl groups, where the stabilization much more strongly affects the unoccupied levels. This can be rationalized on the basis of the molecular orbitals for which we find a much stronger weight on the *p*-*N*,*N*-dimethylamino substituents in the HOMOs and on the *p*-nitro substituents in the LUMOs.

At this stage, two aspects can be emphasized. First, the results of these electronic-structure calculations indicate that the HOMO and LUMO energies of the dioxaborine, oxadiazole, and silole rings can be tuned on the order of 2–3 eV via substitutions as simple as those considered here. Such energy control could potentially allow for the ability to match the Fermi energies of a number of interesting electrode materials. Secondly, the HOMO and LUMO levels for the substituted dioxaborine compounds are consistently more strongly stabilized than their oxadiazole and silole counterparts. These results suggest that dioxaborine-based compounds should exceed oxadiazole- and silole-based systems in both hole-blocking capabilities and overall negative polaron stabilities.

3.2. Electron affinities

The electronic structure analysis given above provides a quantitative comparison of the one-electron energy levels often utilized for energy band diagrams of organic device structures. However, the question arises as to what extent do the molecular orbital energies represent an accurate description of the true electron affinities and, hence, actual energetic barriers for carrier injection (note that since our emphasis here is on molecular design, interface-dipole-related issues are not considered). To that aim, we have compared the trends obtained from the LUMO energies (that in the framework of Koopmans' theorem [23], KT, can be viewed as an approximation to electron affinities) and the differences in self-consistent field energies, ΔSCF, obtained for the neutral and radical-anion states. For this discussion, we deal primarily with vertical electron affinities, which are representative of instantaneous processes. Thus, the energy of the radical-anion is calculated at the resultant neutral equilibrium geometry (it is worth noting that the vertical (adiabatic) electron affinity is defined herein as the energy of the equilibrium neutral geometry subtracted from its energy (energy of the equilibrium radical-anion geometry) on the radical-anion potential energy surface; hence, a negative vertical (adiabatic) electron affinity reflects an energetically stable radical-anion state). Estimations of electron affinities via KT, especially using DFT methods, face a number of potential problems. First, KT neglects energetic effects due to electron reorganization, electron correlation, and vibronic coupling processes [24]. Furthermore, even though Janak's theorem [25] establishes that DFT HOMO and LUMO energies can be regarded as the ionization potential and electron affinities for infinite systems [26], the validity of Koopmans' DFT [27] is questionable following the argument that KT cannot apply to DFT methods since a priori the Kohn-Sham orbital eigenvalues are auxiliary quantities [28]. Regardless of these potential pitfalls, molecular orbital energies have been successfully utilized in predictions of electron affinities [24] and other energetic properties, even at the DFT level [26,28,29]. Additionally, the lower computational cost and the resulting possibility to study increasingly complex systems, and the ability

to (at least partially) include electron correlation into the formalism, make orbital energies obtained from DFT methods even more attractive [26]. It is with this background that we formally evaluate the ΔSCF vertical electron affinities and compare them to molecular-orbital-based estimates for these systems.

Upon initial analysis, the B3LYP/6-31+G*//B3LYP/6-31G*-calculated vertical electron affinities, see Table 2, appear to be very consistent with the trends observed for the LUMO energies; the dioxaborine results compare well with those recently reported by Fabian and Hartmann [18]. For each substitution, the calculated vertical electron affinities for the dioxaborine systems are significantly stabilized versus the oxadiazole and silole counterparts. As is shown in Fig. 5, the correlation between the ΔSCF and the KT-derived electron affinities is in fact excellent for all bis-aryl substituted systems. Linear regression analysis of the points corresponding to the substituted systems provide a linear fit with a slope close to one and an offset of 1.32 eV from a line through the origin. Such a constant offset has been shown previously with Hartree–Fock methods [24] and, in this case, is probably due to a variety of factors including the DFT methodology in general, as well as the choice of exchange-correlation functionals and basis sets. The unsubstituted dioxaborine, oxadiazole, and silole cores, however, somewhat deviate from this linear regression fit. We attribute this error in the KT-derived electron affinities to the smaller electron count in the unsubstituted systems, which can be expected to increase the negative effect of the frozen-orbital approximation on which KT is based.

Overall, this provides credence, especially for the derived trends obtained and discussed above, in the one-electron molecular orbital picture. A question still remains, however, as to the stability of the radical-anions of these compounds versus oxidative electron

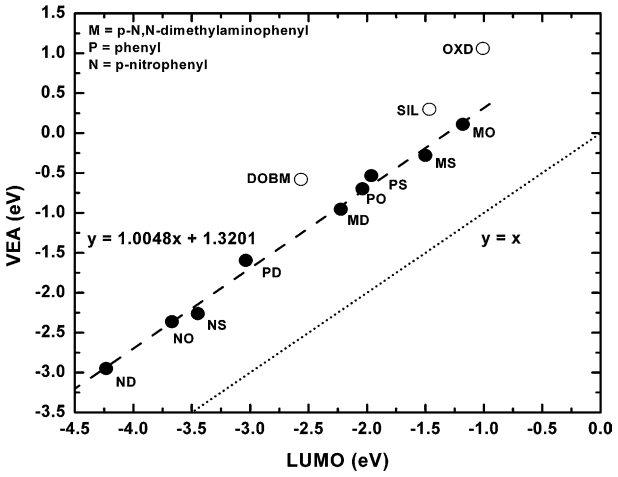

Fig. 5. B3LYP/6-31+G*//B3LYP/6-31G*-derived vertical electron affinities as a function of the LUMO energies. The core rings are represented by open circles, while the substituted systems are represented by filled circles.

trapping by molecular oxygen. The calculated adiabatic electron affinity for molecular oxygen at the B3LYP/6-31+G* level is −0.59 eV; this result is in good agreement with previous DFT results [30,31]. The dioxaborine systems, specifically, favor very well. The calculated adiabatic electron affinity for the dioxaborine ring is −0.92 eV. In the phenyl (−1.82 eV), *p*-*N*,*N*-dimethylaminophenyl (−1.27 eV), and *p*-nitrophenyl (−3.19 eV) systems the radical-anion stability is dramatically increased; thus, it may be expected that electron trapping by molecular oxygen is minimal in devices composed of the dioxaborine systems. Though both the oxadiazole and silole rings possess even slightly positive electron affinities, substitution appears to stabilize the molecular structures preventing oxidative trapping by molecular oxygen; in particular, the

Table 2
Vertical (VEA) and adiabatic (AEA) electron affinity, neutral (λ_1) and radical-anion (λ_2) relaxation energies, and total intramolecular reorganization energy (λ) as determined at the B3LYP/6-31+G*//B3LYP/6-31G* level of theory

Compound	Bis-substituent	VEA (eV)	AEA (eV)	λ_1 (eV)	λ_2 (eV)	λ (eV)
Dioxaborine	Methyl	−0.58	−0.92	0.24	0.34	0.58
	N,*N*-Dimethylaminophenyl	−0.95	−1.27	0.33	0.31	0.64
	Phenyl	−1.60	−1.81	0.11	0.22	0.33
	Nitrophenyl	−2.95	−3.19	0.13	0.24	0.37
Oxadiazole	Hydrogen	1.06	+0.92	0.36	0.14	0.50
	N,*N*-Dimethylaminophenyl	0.11	−0.26	0.36	0.37	0.73
	Phenyl	−0.53	−0.69	0.15	0.15	0.30
	Nitrophenyl	−2.36	−2.54	0.17	0.18	0.35
Silole	Hydrogen	0.30	+0.06	0.29	0.23	0.52
	N,*N*-Dimethylaminophenyl	−0.28	−0.65	0.33	0.37	0.70
	Phenyl	−0.70	−0.95	0.20	0.25	0.45
	Nitrophenyl	−2.62	−2.52	0.21	0.25	0.46

Note that the electron affinities are calculated by subtracting the total energy on the neutral electronic configuration from the energy of the radical-anion electronic configuration.

phenyl and *p*-nitrophenyl substitutions offer significant stabilization.

3.3. Intramolecular reorganization energy

Further information that can be gained from the results of the ΔSCF calculations is the intramolecular reorganization energies upon reduction. The transport properties of negative charge carriers in a (disordered) organic molecular film can be described within semiclassical Marcus theory and extensions thereof as a self-exchange electron-transfer reaction between two neighboring molecules – the acceptor being in the neutral electronic state and the donor in the reduced radical-anion state. Quantum-chemical analysis allows for the description of both the transfer integral (t) and the intramolecular reorganization energy (λ) given by the semiclassical Marcus equation [21]. The estimation of the transfer integral, which is related to the electronic coupling between adjacent molecules, requires detailed knowledge of the molecular packing within the film; in the absence of such structural data, we will not evaluate t here. The intramolecular reorganization energy component of the total reorganization energy (the other component being due to medium polarization in the presence of an excess charge) accounts for the molecular geometry relaxation events coincident with the charge hopping between molecules within the film. The intramolecular reorganization energy combines the relaxation energies of the electron-donor (initially ionized) molecule, λ_2, and of the electron-acceptor (initially neutral) molecule, λ_1, upon electron-transfer reaction (polaron hopping) [32]. It should be noted that for electron-transfer (carrier hopping) rates to be high, reorganization energies should be kept as low as possible.

The DFT-derived intramolecular reorganization energy results vary rather significantly and, for different substituents, range between 0.3 and 0.7 eV, see Table 2. For the unsubstituted systems, the dioxaborine (0.58 eV), oxadiazole (0.50 eV), and silole (0.52 eV) results are very similar. For all three central rings, phenyl substitution provides the smallest overall intramolecular reorganization energy followed by *p*-nitrophenyl, and *p*-*N*,*N*-dimethylaminophenyl; it is worth noting, however, that the difference in reorganization energies between the phenyl and *p*-nitrophenyl substitutions is rather small, on the order of 0.01–0.05 eV. The phenyl- and nitrophenyl-substituted dioxaborine and oxadiazole present reorganization energies on the order of 0.3–0.37 eV; these values are only slightly larger than that calculated [33,34] for the widely studied hole-transport material *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-([1,1′-biphenyl])-4,4′-diamine (TPD), 0.29 eV. They are, however, significantly larger than in pentacene, 0.10 eV [35], which presents a rigid macrocyclic backbone.

4. Conclusions

In summary, the electronic structure, electron affinity, and intramolecular reorganization energy results presented here suggest that dioxaborine-based systems should compare favorably with the already successful electron transport systems based on oxadiazole and silole chemistry. The HOMO and LUMO levels for the bis-substituted dioxaborine species are consistently more strongly stabilized, indicating the possibility for both favorable hole-blocking and electron-injection properties. In addition, the large electron affinities and comparable intramolecular reorganization energies provide further evidence that dioxaborine-based systems should be interesting candidates for electron-transport materials. Finally, it has been demonstrated for all three compounds that small chemical modifications in the molecular structure can allow for the tuning of both the HOMO and LUMO energies over a 2–3 eV range.

Acknowledgements

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