

ABSTRACT

Singlet open-shell ground state molecules are rapidly gaining importance in the recent times due to the possible applications as organic field effect transistors (OFET) and in nonlinear optics (NLO). They are usually characterized experimentally by small HOMO-LUMO gap (HLG) and long wavelength absorption in the UV/visible spectrum. Additionally SQUID measurements on the powdered sample can give us the singlet-triplet (ST) energy difference which would be very small. Theoretical studies using *ab initio* methods would require multideterminants for description hence the wavefunction shows spin contamination when single determinant methods are used. Calculated ST gap would also be less than 1 eV. One such set of molecules are the polycyclic aromatic hydrocarbons. They have the ability to show ambipolar transport in FET due to the small HLG. In the field of NLO they been shown to have large γ values both from experiment and theoretical calculations. The major issue right now in these molecules which has to be overcome before applications in materials is the stability.

Biradicals are molecules consisting of two nearly degenerate non bonding molecular orbitals (NBMO) occupied by two unpaired electrons. They could either have a triplet or Hund's rule violated singlet ground state. Due to this they are highly reactive and unstable. The type of molecules which can find applications in the field of materials is the conjugated biradical molecule. These can be represented by valence bond structures in resonance. Conjugated biradical systems can be broadly divided into two types – Kekule and non-Kekule systems. In some cases the degenerate NBMOs (HOMOs) due to substitutions would have a small energy gap and here the singlet would be more stable but with some biradical character (BRC) retained (partial occupation of LUMO). These types of molecules are called as biradicaloids. Though there is no clear threshold, one could imagine the closed shell molecule at one extreme and the biradical molecule at the other extreme and a biradicaloid anywhere in the middle. Molecules having a small

BRC are of advantage as they are stable and can also show the properties of the biradical described above.

There are many molecules in literature which are derivatives of non-Kekule type biradicals like tetramethylenemethane, tetramethyleneethane, tetramethylenebenzene etc. Introduction of heteroatoms into the rings increases the zwitterionic character thus stabilizing the molecule but retains a small BRC. These molecules can be said to inherit the biradical nature from the parent molecule. In fact the biradicaloid nature of many of these molecules can go unnoticed unless larger exact exchange is included into the density functional for the calculation. The thesis work was initiated by looking into such molecules from literature with two objectives, one to evaluate theoretically such molecules for material applications and the other for understanding the structure and stability to improve these molecules.

This thesis consists of five chapters in which first chapter gives introduction biradicaloid molecules. Subsequent chapters are case studies on each set of molecules and their properties (mainly the linear optical, stability and semiconducting properties).

Chapter 1

This chapter gives a general introduction to biradicaloid molecules. A brief out line of the theoretical/computational methods used for this work is also presented.

Chapter 2

Main factors responsible for the red to near infra red (NIR) absorption of the benzobis(1,2,5-thiadiazole) (**BBT**) derivatives have been investigated using high level computational studies. These molecules with NIR emission are of importance due to the recent reports of possible role in NIR Organic Light Emitting diodes (OLED) development. These molecules are having sulfur diimide bonding and are distinguished from many other compounds by

its non- classical structure. Calculations of these compounds therefore need more sophisticated quantum chemical methods. The electronic structure has been determined using closed-shell/open-shell DFT methods (B3LYP and BHandHLYP). Molecular geometries were calculated using B3LYP and BHandHLYP DFT methods. The obtained results are compared with experimental crystallographic data where available. The wavefunction stabilities of these BBT derivatives have been tested. It is noticed that using the BHandHLYP functional, the wave function becomes instable though large HLG are obtained. On the other hand a stable wavefunction is obtained using the B3LYP functional but the HLG is small. The B3LYP HLG is in good agreement with the available experimental data. Nevertheless results from both functionals indicate a possible LUMO occupation/ biradicaloid character (BRC). Different computational methods are used to quantitatively determine the BRC of the BBT derivatives. It is found that at the DFT level the S–T gaps calculated are less than 20 kcal/mol for the BBT derivatives. The computed CASSCF coefficients also point out to a BRC for the BBT derivatives. It is observed that the BRC has a good correlation with the NIR absorption, smaller the excitation energy-larger the BRC. The transition energies of three known chromophores calculated at the SAC/SAC-CI level of theory were in excellent agreement with the experimental values. Charge transfer (CT) based on Mulliken charges of both ground and excited state are obtained from high level SAC/SAC-CI studies. From this data it is indicated that substantial CT from the side groups to the middle ring is taking place in the **BBT** derivatives. The excitation energies do not have a correlation to this CT. *Ab initio* valence bond studies are carried out for the unsubstituted BBT to predict the relative weights of the individual Lewis structures to the resonance picture. It is concluded that a more general description which include the zwitterionic and biradical structures are necessary for these molecules and not just simple donor-acceptor-donor(D-A-D) structures as suggested in the literature.

Chapter 3

Recent literature reports indicate that derivatives of benzothiadiazole (**BT**) and benzobis(thiadiazole) (**BBT**), which differs from **BT** by an extra thiadiazole ring, exhibit good semiconducting properties like high electron mobility and low lying LUMO levels. In this chapter computational techniques like DFT, spin-flip DFT and valence bond methods are used to analyze the semiconducting properties of these molecules. Calculations at the B3LYP/cc-pVTZ level reveal that all the BBT molecules, including the bare **BBT** ring, have lower lying LUMO energies (3.70 – 4.11 eV) compared to the **BT** derivatives (2.56 – 3.41 eV) with similar substitution. The reorganization energies (λ_+/λ_-), obtained at this level of theory, of the **BT** derivatives are around (225-333)/(246-315) meV while **BBT** derivatives have much smaller reorganization energies and these are in the range (129-259)/(150-230) meV. It is observed here that the different behaviour of BBT is due to the inherited biradicaloid character from the parent molecule tetramethylenebenzene (**TMB**), a disjoint non Kekule biradical having NBMOs as the HOMO and the LUMO. The perturbation of the orbitals of the biradical **TMB** to obtain **BBT** also is the major cause for the BBT derivatives to have a larger EA and smaller HOMO-LUMO gap (HLG) when compared to **BT** derivatives.

Chapter 4

Keeping in view the possible applications of singlet open-shell molecules as semiconductors, non-classical derivatives of the heterocyclic rings benzobis(thiadiazole) (**BBT**) and its positional isomer thiadiazolothienopyrazine (**TTP**) have been characterized using DFT methodologies. M06-2X, B3LYP and BHandHLYP functionals have been used to optimize the geometries and estimate the vertical transition energies. It is observed that unlike BHandHLYP functional (50% exchange) which gives rise to spin contaminated solutions for all molecules in the series, M06-2X (54% exchange) for most of the molecules affords wavefunction either with no instability or negligible instability. The results have been compared with the earlier reported experimental data and those obtained in this work using spin

flip (SF)-5050 method. It is found that B3LYP does not fare well while on the other hand the M06-2X and SF-50-50 are in good agreement with the experimental results. It is seen that M06-2X TD-DFT for the molecules can be carried out without major spin contamination and also the more time consuming CI can be avoided for calculation of transition energies. Biradical nature of the molecules are estimated by singlet-triplet gap. Intramolecular charge transfer is calculated. It is found that the ring substituents donate charge in the ground state creating a zwitterionic structure. Thus the substituents play an interesting dual role, decreasing the stability of the molecule by increasing the biradical character (small HOMO-LUMO gap), and stabilization of this ground state by intramolecular charge transfer.

Chapter 5

Squarines and croconine dyes have oxyallyl biradical substructure and hence inherit the character of the parent biradical (Biradicaloids). Earlier TDDFT studies with different DFT functionals fail to predict the right excitation energies in these molecules. The croconate dyes, however, have larger deviation from the experimentally observed values in all the functionals studied even after inclusion of the solvent effects. The deviations are also not systematic. Biradicaloids with high BRC in general may require multi-reference description to obtain the first vertical singlet-singlet excitation energy. In this chapter detailed electronic structure for a series of croconate molecules with varying BRC is analyzed. It is observed that at the single determinant/RB3LYP level the HLG match the experimental absorption for molecules with high BRC. The stable broken symmetry (BS)-UDFT solutions, which are only slightly lower in total energy yield overestimated HLG due to spin contamination. For medium and small BRC the RB3LYP has stable solutions but the HLG deviates, the deviation being quite large in the latter case. The Spin Flip (SF)-TDDFT/TDA method is used which is known to cover non-dynamical electron correlation in biradicals. Excitation energies calculated using single reference SF-TDDFT methods are in good agreement with the experiment for the molecules with medium-small BRC.