

Computational study of the electronic spectra of some B–N dyes

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Dedicated to Academician Ivan Juchnowski on the occasion of his 70th birthday

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Boron “complexes” of dipyrromethenes (BDP) have found wide application as excellent optoelectronic materials and luminescent chemo- and bio-sensors since the very end of the past century. Their high absorption coefficients and fluorescence quantum yields in the VIS spectral region are augmented by outstanding resistance to photodegradation. Presently, a large amount of empirical, unstructured knowledge on the relationships between molecular structure and spectroscopic parameters of BDP dyes has been accumulated. High level correlated calculations, CISD with size consistency corrections, reproduce fairly well the energies of lowest pyrromethene singlet excited states, but have a prohibitively high computational cost and do not satisfactorily predict substituent effects, Stokes’ shifts, and solvent effects on either absorption or emission.

We apply a recently proven semiempirical CISD AM1 methodology to study excited state energies and substituent effects on pyrromethene chromophores, parallel to TD DFT computations of the Frank–Condon absorption and emission transition energies. This combination of methodologies is a robust approach to the rational search for new compounds within the relatively novel class of boron-containing optical materials.

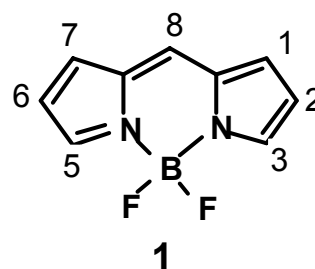
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INTRODUCTION

The search for new classes of heterocyclic compounds as fluorescent indicators and laser dyes is a challenging and rapidly advancing area. Pyrrolo-boraheterocycles such as [2,3-a,5,6-a]bis-pyrrolo-1,1-difluoro-[1,2,6]-boradiazine, or 4,4-difluoro-borindacene **1**, BDP, Scheme 1, [5–7] have a number of convenient properties, in particular an outstanding resistance to photodegradation, high molar absorptivities and high fluorescence quantum yields. BDP dyes have found interesting applications as optoelectronic materials, laser active media and molecular chemo- and bio-sensors. [8–12].

There is indeed some remote topological similarity between borindacenes and triphenylmethane dyes, e.g. rhodamines as well as fluorescein, which has probably contributed to the rapid commercialization of the new heterocycles under the trademark BODIPY® [11, 12], but hardly to the understanding of structural and electronic factors behind the observed photophysical properties. The latter factors have been thoroughly studied with rhodamines, [4] while the introduction of the scarcely known boron atom into the seemingly aromatic [5–12] boraheterocycles renders a wide unexplored area open to imagination and research.

X-ray structural as well as computational studies in general confirm the supposedly aromatic structure of pyrrolo-boraheterocycles [1, 2, 10]. The rather numerous computational papers however provide no detailed description of the nature of the excited states and, in particular, of the fluorescent states. Knowledge of structural changes and electronic distributions of the latter geometry relaxed excited states is necessary for the description of such quantities as emission wavenumbers and Stokes’ shifts. This information could significantly amplify the capacity for rational search for and design of new compounds with promising photophysical and photochemical properties as fluorescent probes for biological assays. Notably, solvent effects on both absorption and emission maxima of BDP are minimal [5–7] and they will not be considered in the present study.



Scheme 1. Structural sketch of the parent 4,4-difluoro-s-borindacene.

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COMPUTATIONAL DETAILS

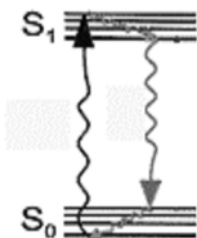
To model the well known electron excitation – emission cycle of Jablonski [3], Scheme 2, we use a computational cycle consisting of the following steps:

1. Semiempirical CISD calculation of the equilibrium geometry of the S_0 electronic state of the molecules with full geometry relaxation.

2. Single point semiempirical CISD, as well as TD DFT calculations of the S_1 energy at the S_0 geometry, relating the results to vertical Frank-Condon $S_0 \rightarrow S_1$ absorption transition energies.

3. Semiempirical CISD calculation of the equilibrium geometry of the S_1 (or, possibly, T_1) electronic state with full geometry relaxation.

4. Single point semiempirical CISD and TD DFT calculations of the S_0 energy at the S_1 (or, possibly, the T_1) geometry and relating the transition energies to the corresponding vertical $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ emission energies.



Scheme 2. The simplified Jablonski cycle, used in the computational modelling.

While having so far used semiempirical AM1 method in all steps of the model computational cycle, we are aware of its deficiencies, in particular its inability to reproduce simultaneously the qualitative trends in substituent and solvent effects on both electronic absorption and emission spectra for any given chemical compound or series of compounds. Apparently the same situation exists also with TD DFT or TD HF or nonempirical MO CIS calculations of electronic spectra [4]. The reasons for the present computational situation are clear: absorption spectra can be routinely reproduced as vertical electron excitation energies from the ground molecular electronic states. However, CIS and TD DFT geometry optimizations of excited electronic states are troublesome and unreliable due to their multireference nature [4]. Therefore, we take the liberty to carry out semiempirical CISD geometry optimizations of electronic states of interest, and use TD DFT at the latter semiempirical geometries to obtain the vertical transition energies for electron excitation as well as emission processes. The calculated TD DFT energies for the ground and lowest excited molecular electronic states are corrected for dynamic

electron correlation using the recently introduced double-hybrid functional B2PLYP [13], which uses the “resolution of identity” methodology to introduce perturbational MP2 corrections to the standard generalized gradient (GGA) DFT energy [13, 14]. All CISD AM1 computations are performed with MOPAC 93 with c.i. = 5 open (2,2) EF for the semiempirical geometry optimizations [15]. Despite the semiempirical nature of AM1, CISD geometry optimizations are still very laborious. We persisted with the optimization process until reducing the calculated gradient norm below 1 kcal/Å or radian. For the TD B2PLYP 6-311++G(2d,2p) single point energy calculations we use ORCA [16] at the optimized AM1 geometries.

RESULTS AND DISCUSSION

Electronic transition energies of medium size molecules are so far among the most problematic properties to reproduce by quantum mechanical calculations, giving at best a precision of e.g. 0.2 eV for electronic absorption energies, and in quite a few cases much worse [17]. Recent high basis set level TD DFT computations have shown convergence to significantly better precision, e.g. below 0.05 eV relative to the experiment, using augmented triple zeta basis sets and explicit treatments of solvent effects on electron transition energies [17]. The computational cost of these calculations is however still too high for routine screening of large batches of essentially unknown heterocyclic structures for the desired photophysical and photochemical properties. Our goal is rather a pragmatic search for a satisfactory, robust approach for the prediction of electronic absorption and emission energies, as well as their solvent dependence. Such an approach, a methodology or combination of methodologies, would ultimately lead to the ability to rationalize the search for new molecules with suitable photophysical and optoelectronic properties.

A prerequisite condition for the use of combined computational methodologies as rational search tools is the consistency of computed molecular parameters. In the present case, we note that CISD AM1 and B3LYP/6-31G* geometries of borindacene derivatives are reasonably close, with bond length differences usually below 0.02 Å, Fig. 1. For the shown borindacene derivative, the only more significant differences in calculated bond lengths between AM1 and B3LYP/6-31G* are for B–N, 1.645 vs. 1.562 Å, and B–F, 1.344 vs. 1.392 Å. The calculated rotation angle of the 8-aryl fragment relative to the borindacene is 56° (AM1), resp. 53°, (DFT).

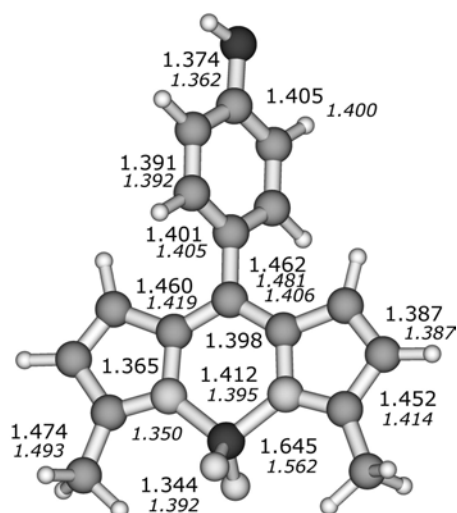


Fig. 1: CISD AM1 and B3LYP/6-31G* (*italics*) ground state geometries of 8-[4'-hydroxyphenyl]-4,4-difluoro-*s*-borindacene. Bond lengths are given in Å.

Some understanding of the nature of electronic transitions in 8-aryl-BDP dyes can be gained by

comparison of their geometries in the ground S_0 and excited S_1 electronic states. Bond length values calculated at the CISD AM1 semiempirical MO level are compared in Fig. 2 for the 4'-hydroxy-phenyl derivative. In the S_1 geometry of the aryl fragment one observes some indication of bond length redistribution typical of intramolecular charge transfer (ICT) dye molecules. However, these changes do not clearly characterize the underlying electron density redistribution taking place upon excitation from the S_0 to the S_1 state. Computed CISD AM1 atomic point charges of the ground S_0 and excited S_1 state are shown in Fig. 3.

Similar to geometry changes, the point charge redistribution in case of S_0 – S_1 excitation does not clearly reflect the ICT pattern, widely discussed in relation to traditional dyes [6, 10]. Therefore, to clarify the nature of the lowest energy electron excitations in 8-aryl borindacenes, we consider explicitly the molecular orbitals taking part in the process (Fig. 4).

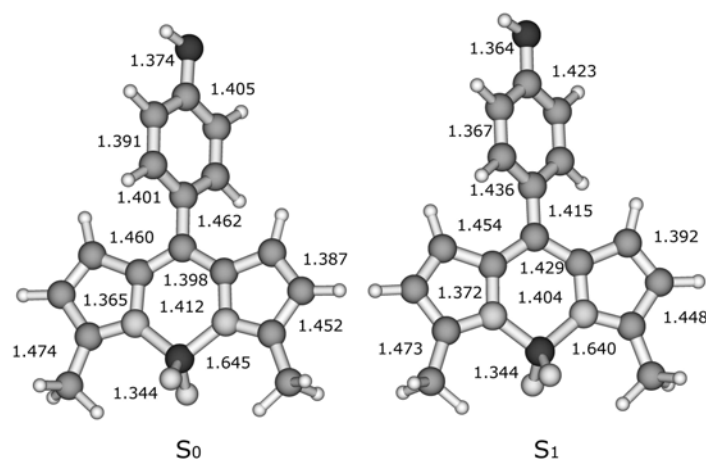


Fig. 2. CISD AM1 ground S_0 and first excited S_1 singlet state geometries of 8-[4'-hydroxyphenyl]-4,4-difluoro-*s*-borindacene. Bond lengths are given in Å.

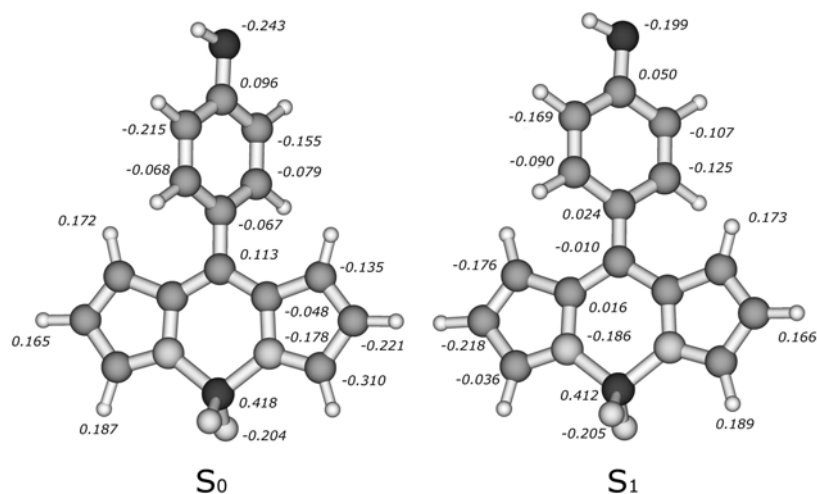


Fig. 3. CISD AM1 atomic point charges of 8-[4'-hydroxyphenyl]-4,4-difluoro-*s*-borindacene in the ground S_0 and first excited S_1 singlet states.

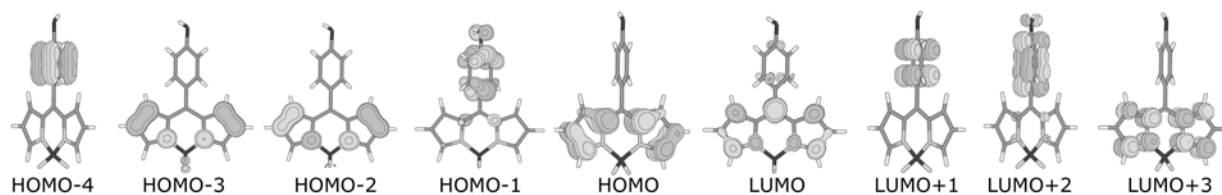
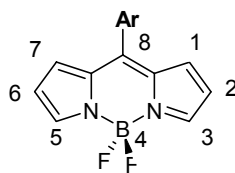


Fig. 4. Molecular orbitals of 8-[4'-hydroxyphenyl]-4,4-difluoro-borindacene, taking part in lowest electronic excitations. The approximate C_{2v} symmetry is apparent.

Table 1: Longest wavelength absorption and fluorescence emission maxima (ν) of 8-aryl substituted 3,5-dimethyl-4,4-difluoro-s-borindacenes, together with the respective Stokes' shifts ($\Delta\nu$) in cyclohexane [5–7] and calculated vertical electron transition energies (E), 10^3 cm^{-1} . Also given are the fluorescence quantum yields ϕ and theoretical oscillator strength F , derived from the B2PLYP/6-311++G(2d,2p) calculations.



Aryl	ν_{abs}	ν_{em}	$\Delta\nu$	ϕ	E_{abs}		F	E_{em}		F
					AM1	B2PLYP		AM1	B2PLYP	
	19.53	19.08	0.447	0.29	23.85	24.15	0.80	19.69	22.35	0.68
	19.53	19.05	0.484	0.25	23.60	24.12	0.81	19.30	22.18	0.67
	19.53	19.08	0.556	0.17	25.43	24.05	0.78	21.00	22.03	0.61
	19.69	19.31	0.454	0.15	24.89	24.02	0.76	18.59	22.65	0.66
	19.61	19.19	0.414	0.42	24.60	23.95	0.74	20.09	22.75	0.80
	19.61	19.19	0.414	0.45	24.60	24.29	0.81	20.19	22.85	0.69
	19.42	18.76	0.656	0.073	23.70	23.81	0.78	19.45	21.12	0.60
	19.34	18.55	0.789	0.038	23.78	23.66	0.77	19.14	21.00	0.59

TD DFT calculations reveal a common characteristic of all three computed lowest singlet excited states. In all the 8-aryl-4,4-difluoro-borindacene molecules investigated computationally these states are dominated by electron excitations from consecutive highest occupied orbitals to the lowest unoccupied orbital. The corresponding CI expansions are regularly dominated up to 90% and more by excitations from HOMO to LUMO, S_1 ; from HOMO-1 to LUMO, S_2 ; and from HOMO-2 to

LUMO, S_3 , Fig. 4. Orbital distributions of the three highest occupied MO's together with the LUMO, also reveal a relatively little absolute dipole moment change upon corresponding electron excitations, but significant change of dipole moment directions.

Substituents at position 8 of 4,4-difluoroborindacenes preserve the C_{2v} local symmetry of the parent molecule and thus provide a clear insight into the nature of electronic transitions. $S_0 \rightarrow S_1$ excitation in BODIPY® molecules is accompanied by

intense electron density reorganization from peripheral pyrrolic fragments towards the local C_2 symmetry axis and, in the case of π -electron withdrawing substituents as CN and COOCH₃ in the 8-aryl fragment, also to the electron acceptor substituent along the same twofold symmetry axis. This explains the calculated high oscillator strengths for the lowest energy excitations of these compounds and the observed high molar absorptivities [6, 10].

Particularly revealing are the predicted in agreement with experiment substituent effects on absorption and emission Frank-Condon transition energies, Table 1. Electron withdrawing substituents in the aryl fragment at position 8 stabilize the S_1 excited state by drawing the electron density to the central bora-heterocycle, thereby shifting both the $S_0 \rightarrow S_1$ and the $S_1 \rightarrow S_0$ electronic transitions in the direction to the red. Vice versa, π -electron donating substituents in the aryl fragment at position 8 destabilize the S_1 state by drawing electronic density away from the symmetry axis, which results in a blue shift of the electronic transitions. Due to the nonplanar arrangement of 8-aryl substituents relative to the borindacene, the mentioned electronic effects are relatively small. Nevertheless, the above observations are completely opposite to the traditional electronic substituent effects on the absorption or emission Frank-Condon energies of classical ICT organic chromophores like 4-dimethylaminobenzonitrile, or 2-propionyl-6-dimethylamino-naphthalene, PRODAN [1].

The results in Table 1 clearly reflect the trends outlined above based on considerations of BODIPY® orbitals. However, calculated absorption Frank-Condon energies are higher than experimental values by roughly 0.5 eV, or ca. 4000 cm⁻¹, i.e. a much worse result than recent B3LYP and PBE0 predictions [17]. This failure of single point TD B2PLYP/AM1 calculations to predict electronic absorption spectra is possibly due to obsolete boron atom parameterization in the original version of AM1 [18], now abandoned in the recent versions of MOPAC and superseded by PM3 and PM6 [15, 19]. Another possible reason for the faulty representation of BODIPY® ground electronic states may be the inability of semiempirical calculations to represent B–N bonding and its participation in the π -electronic system of borindacenes correctly. The latter conjecture is based on the fact that the largest discrepancy between AM1 and B3LYP/6-31G* geometries of borindacenes, almost 0.1 Å, refers exactly to the B–N bond length. Further complete B2PLYP studies of borindacenes will certainly bring clarity to this point.

A considerably better relationship is obtained between theoretical B2PLYP/6-311++G(2d,2p)//CISD AM1 and experimentally

observed emission Frank-Condon energies, Fig. 5. While the absolute differences between the latter values and calculated $S_1 \rightarrow S_0$ vertical transition energies are still high, in the range of 0.3 eV (2500 cm⁻¹) and the slope of the linear relationship is relatively high, the vanishing intercept certainly indicates that CISD AM1 geometries of the emitting state, S_1 in the case of BODIPY®, represent qualitatively correctly the structural changes upon excitation. This result is another argument in favour of our computational approach in modeling the “simplified Jablonsky cycle”, Scheme 2, in the spectroscopic and theoretical study of molecular excited electronic states.

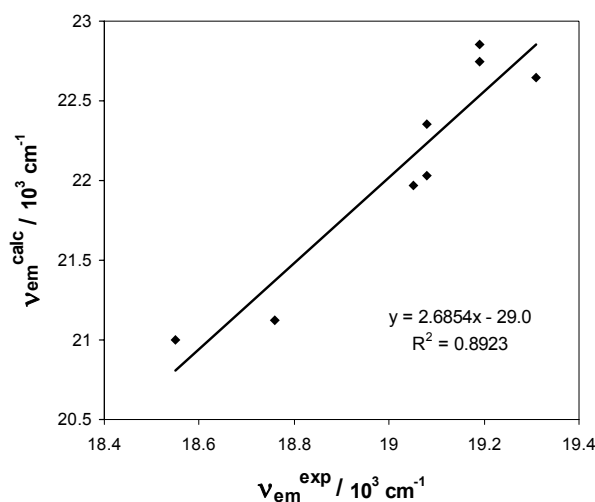


Fig. 5. The linear relationship between experimental and calculated single point B2PLYP 6-311++G(2d,2p)//CISD AM1 fluorescence emission energies.

Apparently, one more argument in the favour of our “reduced model of Jablonsky cycle” is the predicted dual emission of 8-[4'-dimethylamino-phenyl]-4,4-difluoro-borindacene, coming from closely lying adjacent S_1 and S_2 excited electronic states (Table 1). As it was stated in the above orbital analysis, the S_2 state is dominated by the HOMO-1 to LUMO excitation, Fig. 4, and should thus be a true charge transfer electronic state. Dual fluorescence of 4'-aminophenyl borindacenes has indeed been observed experimentally [6], the relative intensity of the two bands depending on the solvent and certainly deserving further more detailed theoretical analysis.

CONCLUSION

A satisfactory linear relationship between calculated single point B2PLYP/6-311++G(2d,2p)//CISD AM1 $S_1 \rightarrow S_0$ emission energies and experimental fluorescence Frank-Condon energies of B–N containing 8-aryl-4,4-difluorobora-*s*-indacene dyes, BODIPY®, is in favour of the qualitative correctness of our recently introduced computational

approach modeling a “simplified Jablonsky cycle” to study structures and energies of excited molecular electronic states. However, in the studies of atypical B–N molecules at the boundary between organic and inorganic species, failure of semiempirical descriptions of corresponding ground electronic states cannot be excluded.

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ИЗЧИСЛИТЕЛНО МОДЕЛИРАНЕ НА ЕЛЕКТРОННИТЕ СПЕКТРИ НА НЯКОИ БАГРИЛА, СЪДЪРЖАЩИ ВРЪЗКАТА B–N

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(Резюме)

Борните „комплекси“ на дипирометени, БДП, намират широко приложение като превъзходни оптоелектронни материали и луминесцентни хемо- и биосензори от самия край на миналия век. Те имат високи моларни абсорбционни коефициенти и флуоресцентни квантови добиви във видимата област, както и изключителна фотостабилност. Досега е натрупан голям обем емпирични неструктурирани факти за връзката между молекулна структура и спектроскопски параметри на БДП багрила. Пресмятанятията на високо ниво, CISD с корекции за съразмерност на вълновите функции, отчитат задоволително енергиите на най-ниските синглетни възбудени състояния на пирометени, но имат твърде висока цена в изчислителни ресурси и не възпроизвеждат ефектите на заместителя, Стоксовите отмествания и ефектите на разтворителя както върху абсорбцията, така и върху емисията.

Ние прилагаме един наскоро въведен полуемпиричен CISD AM1 подход за изчисляване на енергиите на възбудените състояния и ефектите на заместителя при пирометенови хромофори, съвместно с TD DFT пресмятания на енергиите на Франк-Кондоновите абсорбционни и емисионни преходи. Това съчетание на методики е удобен подход за рационално търсене на нови съединения в сравнително новия клас борсъдържащи оптични материали.