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FAST *VS* ACCURATE: EVALUATING TD-DFTB FOR LARGE-SCALE SCREENING OF ORGANIC DYES

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The effectiveness of the semi-empirical TD-DFTB (Time-Dependent Density Functional Tight Binding) method in reproducing the spectral properties of organic dyes was investigated using the example of a library of isomers of the thiophene-containing donor-acceptor Effenberger dye, known for its pronounced solvatochromism. The aim of the work was to find out how suitable the accelerated TD-DFTB approach is for modern molecular design tasks, with a necessity to quickly and reliably identify compounds with intense electronic transitions in the long-wavelength region of the UV-Vis spectrum. The library contained 60 structures in which the positions of the donor (N,N-dimethylamine) and acceptor (NO_2) substituents, as well as the degree of planarity of the π-framework, were systematically varied. For each isomer, the geometry was first optimized at the DFTB level, after which the excitation energies were calculated using the TD-DFTB method. The obtained values were compared with TD-DFT calculations (B3LYP and CAM-B3LYP functionals) performed with geometries, obtained both at DFT and DFTB methods. Such a hybrid scheme significantly reduces the computational costs, allowing screening of large libraries without losing the accuracy. The correlation between excitation energies calculated by TD-DFTB and TD-DFT is given. As obtained, TD-DFTB tends to systematically underestimate the excitation energies, but largely reflects compounds with minimal excitation energies and large oscillator strengths, which makes it a reliable tool for initial screening. Several isomers with long-wavelength absorption and sufficient transition intensity were identified, which are promising for further modification. Thus, TD-DFTB in combination with TD-DFT on optimized DFTB geometries demonstrates an optimal balance between accuracy and speed for prescreening donor-acceptor dyes with given spectral parameters, which significantly enhances the capabilities of rational design of functional organic materials.

Keywords: molecular screening, organic dyes, TD-DFTB, TD-DFT, donor-acceptor systems, long-wavelength absorption.

Introduction

New advances in organic dyes, in particular their spectral characteristics, are of primary importance for the development of photonics and organic electronics. One of the key conditions for rational design of new functional materials, i.e., solar cells, light-emitting diodes and lasers, is effective evaluation and prediction of spectral characteristics, which makes sophisticated optimizing dyes with desired applications possible.

Screening of organic molecules in order to search for systems with specific properties is one of the typical tasks of modern chemistry. Chemoinformatic approaches are widely used to search for molecular systems with desired properties of biological activity [1, 2]. However, the use of chemoinformatic methods to search for systems with specific spectral properties is still an open problem. The difficulties of such work are primarily related to the need to make fast approximate estimates of spectral properties, which may pose a certain problem for large samples of molecules that include dozens of heavy (non-hydrogen) atoms. Among the most common methods for this is time-dependent density functional theory (TD-DFT) [3], which allows for detailed simulation of electronic excitations, based on solutions for electron density that depends upon time. The computational cost demanded for this process severely limits the possibility for large-scale screenings required for the identification of structures with desired behavior. The time-dependent density functional based tight binding (TD-DFTB) method [4] is a promising alternative, as it allows for a significant reduction in computational costs by approximating some integrals using pre-parameterized values. Despite its computational advantages, the ability of the TD-DFTB method to predict the spectral properties of organic dyes remain to further evaluation. An important role in the creation of dyes with desired properties is played by structural isomers, since small changes in the structure can significantly change their electronic structure and spectral characteristics. Therefore, the aim of this work is to compare the efficiency of TD-DFTB and TD-DFT methods using the example of the Effenberger dye [5] isomer library, a thiophene-containing donor-acceptor system characterized by pronounced solvatochromism. To achieve this goal, isomeric library screening at the stage of preliminary selection of candidates with the desired properties is conducted using TD-DFTB method implemented in the DFTB+ package [6, 7], followed by benchmarking calculations using TD-DFT (B3LYP and CAM-B3LYP functionals).

Calculation details

This study centers on a specialized library of compounds generated with the aid of the QUASAR software package, developed in our previous work [8-11]. While preliminary findings were presented in [12], the present study offers a detailed evaluation of the TD-DFTB method's accuracy in predicting the electronic spectra of molecules from the aforementioned library. The library consisting of 60 isomers of the Effenberger dye (Fig. 1). The structures of isomers were generated by construction of key building blocks, two thiophene rings with dimethylamino- and nitro- groups as donor and acceptor substituents. All isomers in the structurally diverse while chemically consistent library are considered as potential in revealing pronounced solvatochromism effects as donor-acceptor π-conjugated systems.

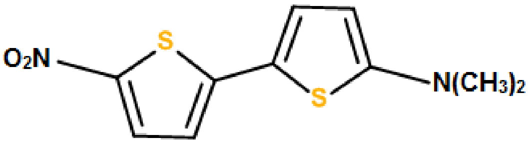


Figure 1. The structure of Effenberger Dye.

The TD-DFTB method was applied in the implementation of the DFTB+ software package [6, 7] which has been incorporated in our QUASAR software package. For the parametrization of the Hamiltonian, we used several sets of the Slater-Koster parameters, available from open source, covering the necessary elements (H, C, N, O, S): 3ob-3-1, auorgap-1-1 and mio-1-1 [13, 14].

Standard TD-DFT calculations were performed using the B3LYP and CAM-B3LYP functionals with cc-pVDZ basis set. The B3LYP functional was chosen as a widely verified compromise between accuracy and speed, while the CAM-B3LYP as supposed allows for a better description of charge-transfer states, which is critical for donor-acceptor systems with pronounced solvatochromism. Calculations were performed using the Gaussian 09 quantum chemistry package [15].

The evaluation of the obtained spectra was carried out by comparing the positions of the longest-wavelength absorption band (λ_{max}) alongside with corresponding oscillator strengths (f), with the energy difference (ΔE) and the correlation between the spectral trends, predicted by TD-DFTB and TD-DFT as main metrics.

Results and discussion

Distribution of Excitation Energies and Oscillator Strengths. The range of excitation energy values obtained for the Effenberger dye isomers calculated by TD-DFT and TD-DFTB methods is presented in the Fig. 2. For the reference structure, the Effenberger dye, following values of TD-DFT excitation energy were obtained (the value of oscillator strength are given in parentheses): CAM-B3LYP – 3.25 eV (0.71), B3LYP – 2.82 eV (0.63). At the same time for the method TD-DFTB based at different parametrization (3ob-3-1, auorgap-1-1 and mio-1-1) we obtained the value 2.89 eV (0.67). For the particular molecule the TD-DFTB method reproduces the corresponding HOMO→LUMO transition quite accurately in terms of excitation energy and transition intensity compared to B3LYP. In addition to the reference structure, high spectral similarity with $\Delta E < 0.1$ eV was obtained for a number of structures (Fig. 3) and is presented in table 1. The structures are listed in order of decreasing oscillator strength, allowing to clearly link the absorption intensity with the structure modification. The highest values of oscillator strength are obtained for structures 1-3, in which the donor and acceptor substituents are located in different thiophene rings, contributing to better conjugation and enhanced intramolecular charge transfer (ICT) upon excitation, which occurs in such structures to a greater extent, as shown by corresponding molecular orbitals in fig. 4. A decrease in the planarity of the molecule, which is quantitatively reflected by an increase in the dihedral angle between the fragments is accompanied by a decrease in the oscillator strength. Thus, the maximum value of the dihedral angle between the planar fragments, at which relatively intense electronic transitions are still obtained in the long-wavelength region of the spectrum, is 26° (structure 3). This indicates a certain permissible limit of curvature of the π-system, at which the effective conjugation remains sufficient to maintain intense absorption.

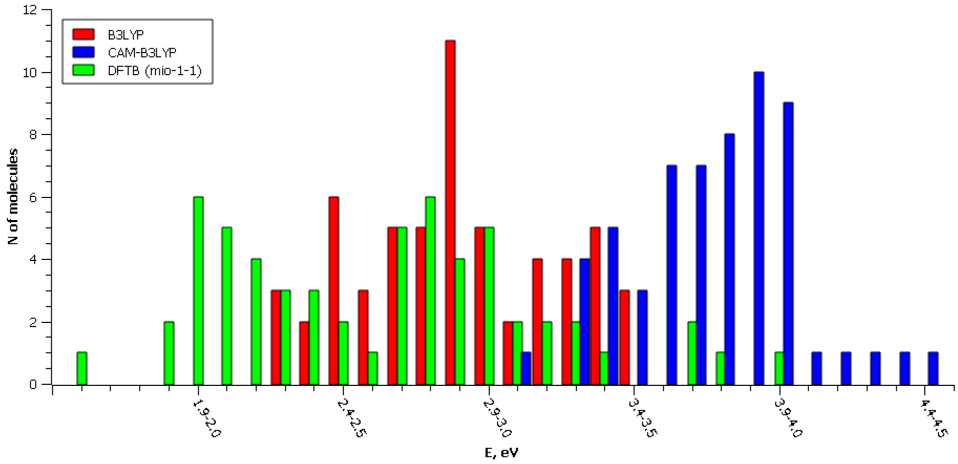


Figure 2. Histogram of excitation energy distribution obtained for the Effenberger dye isomers.

Table 1. Excitation energies (eV) obtained by TD-DFTB and B3LYP for selected isomers of the Effenberger dye (1). Oscillator strengths are given in parentheses.

	B3LYP	3ob-3-1	auorgap-1-1	mio-1-1		B3LYP	3ob-3-1	auorgap-1-1	mio-1-1
1	**2.82 (0.628)**	**2.89 (0.675)**	**2.89 (0.661)**	**2.89 (0.660)**	6	3.15 (0.070)	-	3.13 (0.083)	3.13 (0.084)
2	2.75 (0.378)	2.73 (0.408)	2.77 (0.413)	2.77 (0.412)	7	2.89 (0.039)	2.76 (0.081)	2.82 (0.087)	2.82 (0.087)
3	2.87 (0.281)	2.86 (0.296)	2.89 (0.440)	2.88 (0.439)	8	2.99 (0.017)	2.94 (0.038)	2.96 (0.046)	2.96 (0.046)
4	3.33 (0.184)	3.68 (0.482)	3.38 (0.165)	3.38 (0.165)	9	3.05 (0.016)	2.99 (0.051)	2.96 (0.051)	2.96 (0.051)
5	3.17 (0.136)	-	3.20 (0.145)	3.20 (0.144)	10	2.54 (0.013)	2.56 (0.066)	2.58 (0.077)	2.58 (0.077)

To describe the planarity of molecular systems, in the present article we propose using the average deviation of heavy (non-hydrogen) atoms from the best-fit plane through their coordinates as a quantitative index INP. The best fit plain

$$\beta_0 + \beta_x x + \beta_y y + \beta_z z = 0 \tag{1}$$

was obtained by minimizing the orthogonal distances of heavy atoms, following the principles of orthogonal distance regression.

$$\beta = \arg\min_{\beta}\left(\beta^{+} A^{+} A \beta / \beta^{+} E \beta\right) \tag{2}$$

In this context, $\beta = \left(\beta_0, \beta_x, \beta_y, \beta_z\right)$ defines the parameters of the plane, matrix A contains the atomic coordinates, and matrix E is close to the identity matrix (however $E_{11} = 0$). The matrices are given below:

$$A = \begin{pmatrix} 1 & x_1 & y_1 & z_1 \\ 1 & x_2 & y_2 & z_2 \\ \dots & \dots & \dots & \dots \\ 1 & x_N & y_N & z_N \end{pmatrix}, \quad E = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \tag{3}$$

To solve equation (2), we use the steepest descent iterative procedure. For the molecular library under consideration the value INP deviates from 0Å for planar system to 0.79Å for maximum unplanar.

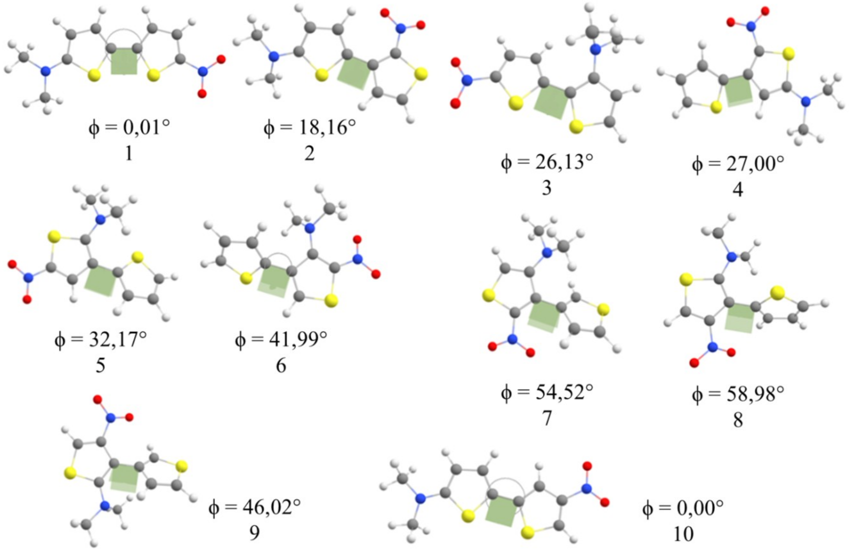


Figure 3. Structures of Effenberger dye isomers for which the best agreement between TD-DFTB and TD-DFT was obtained ($\Delta E < 0.1$ eV). Dihedral angles ϕ are given, according to B3LYP.

Structure 10 (fig. 5) noticeably deviates from the general trend. The structure is planar, with a dihedral angle between the planes of the thiophene rings close to 0°, and spatially separated donor and acceptor groups. However, no intense electronic transition is obtained in the long-wavelength region of the spectrum for this molecule.

Two different parameter sets, auorgap-1-1 and mio-1-1, used for TD-DFTB calculations, give almost identical results. The differences between them are insignificant: the excitation energies differ, as a rule, in the second decimal place (±0.01–0.02 eV), and the oscillator strength values in the third (±0.001–0.005). Nevertheless, for individual structures, presented in fig. 6, the TD-DFTB approach with some types of the Slater-Koster parameters does not predict excited states corresponding to the HOMO→LUMO transition, which, on the other hand, is clearly visible in TD-DFT calculations with energies in the range of 3–4 eV. Among them are molecules characterized by a deviation from overall planarity of 10-60° for the dihedral angle between the planes of two thiophene rings. Among the rejected structures are both those that, according to TD-DFT data, demonstrate low absorption intensity ($f < 0.1$), and those that have large oscillator strength values ($f > 0.2$). This indicates that simplified parameterizations in TD-DFTB can lead to the loss of potentially relevant structures. Therefore, in high-throughput screening, it is advisable to use several independent sets of parameters to minimize the probability of missing promising structures.

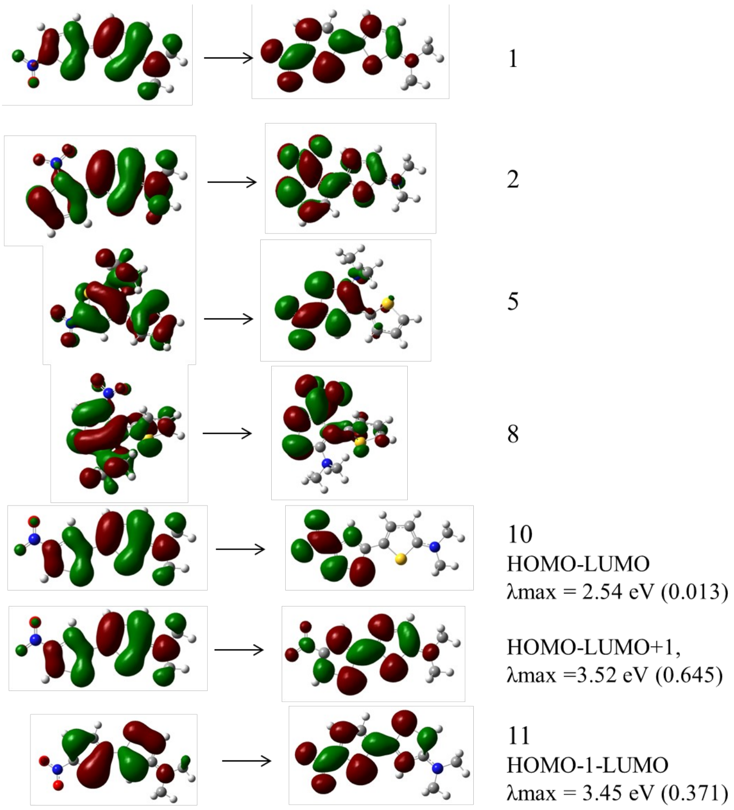


Figure 4. Molecular orbitals, corresponding to the HOMO → LUMO transition for selected structures.

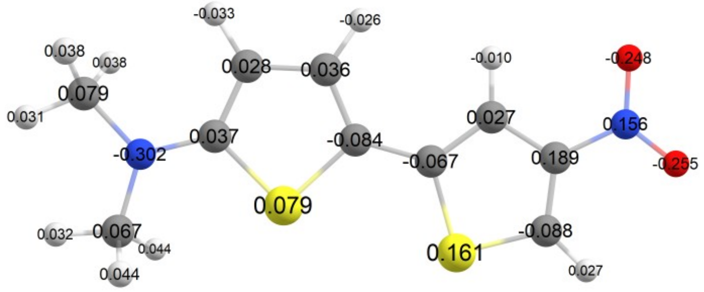


Figure 5. Mulliken distribution of partial atomic charges for structure 10.

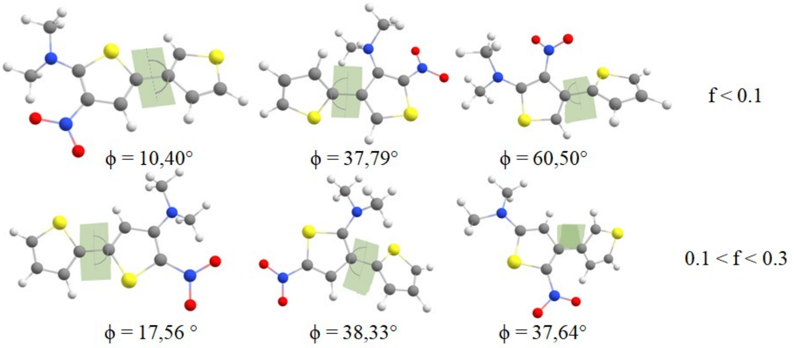


Figure 6. Isomers unidentified by TD-DFTB due to the absence of the predicted HOMO–LUMO transition in absorption spectrum. Dihedral angles and oscillator strength range are given, according to TD-DFT.

Quantitative Comparison. To quantify the agreement between TD-DFTB and TD-DFT for the entire isomer library, several statistical metrics based on the excitation energy values obtained are presented in Table 2. In particular, the coefficient of determination (R^2), which reflects the degree of linear correlation between the samples; the root mean square deviation (RMSD), which characterizes the absolute difference in values; and the asymmetry index (A), which allows assessing the presence of a systematic shift between the data sets.

$$RMSD = \sqrt{\frac{\sum\left(E_{T\,calc} - E_{T\,ref}\right)^2}{n}} \tag{4}$$

$$A = \frac{\sum\left(E_{T\,calc} - E_{T\,ref}\right)}{n} \tag{5}$$

Table 2. Match metrics between TD-DFTB and TD-DFT results for excitation energies.

	CAM-B3LYP			B3LYP		
	3ob-3-1	auorgap-1-1	mio-1-1	3ob-3-1	auorgap-1-1	mio-1-1
R	0.05	0.05	0.04	0.682	0.681	0.691
A	-1.17	-1.12	-1.11	-0.28	-0.25	0.05
RMSD	1.34	1.28	1.27	0.51	0.47	0.47

Due to its long-range correction, the CAM-B3LYP functional, supposed for better description of charge-transfer excitations, tends to overestimate the energy of HOMO-LUMO gap, compared to other hybrid functionals such as B3LYP. Better reproduction of the values is obtained at the B3LYP level (RMSD ≈ 0.5 eV). Nevertheless, qualitative agreement in reflecting the variations in excitation energy depending on the change in the isomer structure is insufficient, confirmed by correlation coefficient $R^2 < 0.5$ for entire library. Linear approximation of the longest wavelength values obtained by TD-DFT and TD-DFTB is shown in the fig. 7 with corresponding equations:

$$\lambda_{B3LYP} = 0.338\,\lambda_{3ob-3-1} + 1.832 \tag{6}$$

$$\lambda_{B3LYP} = 0.409\,\lambda_{auorgap-1-1} + 1.770 \tag{7}$$

$$\lambda_{B3LYP} = 0.424\,\lambda_{mio-1-1} + 1.739 \tag{8}$$

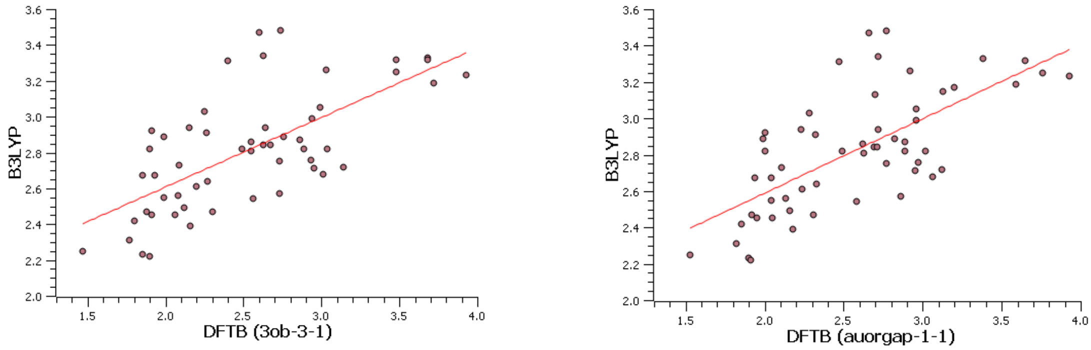


Figure 7. The linear approximation of energy values (eV) calculated using TD-DFT and TD-DFTB approaches.

Analysis of Selected Structures. To assess the extent to which the geometric parameters obtained in TD-DFTB affect the predicted spectral characteristics, we created a sample of 13 structures characterized by relatively intense absorption bands of HOMO-LUMO transition (f = 0.116-0.378, 0.628). For these compounds, additional calculations were performed at the B3LYP/cc-pVDZ level using optimized geometries obtained by the TD-DFTB method and relevant statistical metrics are given in Table 3. It can be observed that the use of such a hybrid approach does not lead to a significant increase in the accuracy of reproducing the absolute values, however, provides improved qualitatively reflection of relative energy changes during the transition from isomer to isomer, as shown in fig. 8. For some structures, the hybrid approach resulted in a significant improvement in the absorption energy reproduction compared to calculations based on the original geometries. In particular, this applies to structures 2 and 4, and structures 11 and 12, characterized by intriguing long-wavelength transitions at relatively low energies. Also interesting spectral properties were found for compounds 13 and 14 (fig. 9).

Table 3. Match metrics between TD-DFTB and TD-DFT results for selected structures.

	B3LYP			B3LYP with TD-DFTB geometry		
	3ob-3-1	auorgap-1-1	mio-1-1	3ob-3-1	auorgap-1-1	mio-1-1
R^2	0.625	0.530	0.526	0.746	0.701	0.703
A	0.02	0.05	0.03	0.03	0.02	0.04
RMSD	0.25	0.32	0.26	0.33	0.28	0.31

The most intense transitions in the long-wavelength part of the spectrum were eventually found for compounds 2 and 12. These molecules are distinguished by spatially separated and located on different thiophene rings donor and acceptor groups, which contributes to more efficient charge transfer upon excitation and the same dihedral angle between the key fragments being about 20°, which suggests that a certain curvature of the molecule, provided that a favorable electron distribution is maintained, does not interfere, and sometimes even promotes, an intense transition in the long-wavelength region. For compound 11, as in the case of compound 10, a more intense electronic transition is observed in the short-wavelength part of the spectrum (fig. 4). This indicates that, despite the presence of donor-acceptor fragments and the planarity of the structure, the nature of the electron density distribution does not contribute to effective charge transfer at lower energies.

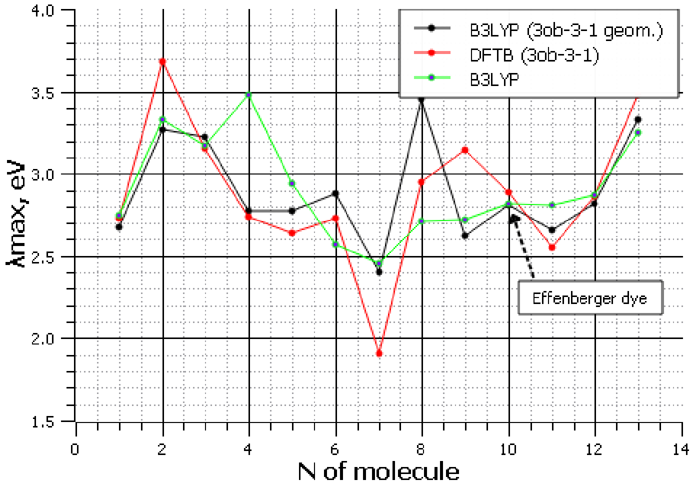
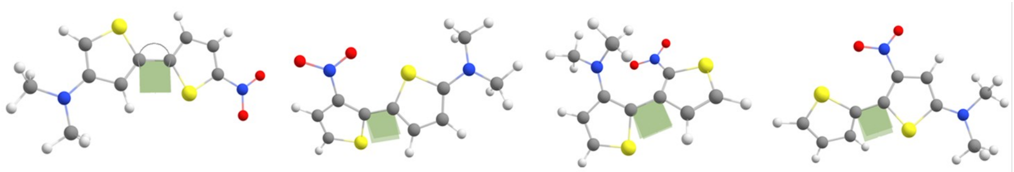


Figure 8. Variations of electronic excitation energies in molecules from the Library C



11	12	13	14
ϕ = 0,00°	ϕ = 16,96°	ϕ = 43,28°	ϕ = 24,89°
λmax = 2,45 eV (0,156)	λmax = 2,72 eV (0,306)	λmax = 2,57 eV (0,116)	λmax = 2,71 eV (0,143)

Figure 9. The structures for which absorption in the long-wavelength region is predicted. Transition energies and oscillator strengths are given according to B3LYP.

Applicability of TD-DFTB for High-Throughput Screening. The evaluation of the applicability of the TD-DFTB approach for preliminary screening of structural library shows that it is an effective tool for identifying compounds with potentially intense transitions in the long-wavelength part of the spectrum. At the same time, the results emphasize the need for individual analysis of structures, since some features of the geometry or electronic structure may remain “invisible” depending on the chosen set of Slater-Koster parameters. The use of several parameterization options is advisable, since although most of the obtained values are close to each other, each set has its limitations and selectively “does not see” certain molecules, in particular those of interest as dyes.

As can be seen from fig. 8, TD-DFTB satisfactorily reproduces the relative changes in transition energies for a number of structures, allowing to estimate the influence of structure modification on spectral properties. However, for individual compounds, such as 2 and 12, exhibiting the lowest absorption energies, the accuracy of TD-DFTB decreases significantly, which requires adjustment of the results. B3LYP refinement of transition energies for geometries optimized at the TD-DFTB level demonstrates improvements in correlation with the reference level of theory, allowing for significant computational savings: while geometry optimization at the DFTB level takes only minutes, at the DFT level it requires days.

Conclusion

The effectiveness of the TD-DFTB approach for predicting the spectral properties of dyes based on the Effenberger dye isomers library was investigated. It was shown that TD-DFTB is capable of qualitatively reproducing the main trends in the transition energy changes during structural modification of molecules, in particular for systems with spaced donors and acceptors. Despite a certain systematic error in the absolute values, TD-DFTB allows for the rapid and low computational cost identification of promising structures with intense transitions in the long-wavelength region of the spectrum.

The proposed hybrid approach, combining geometry obtained with DFTB and transition energies at the B3LYP level, provides a balance between accuracy and computational speed and is a promising tool for the initial screening of a large number of structures. The results demonstrate that TD-DFTB can be an effective method in organic dye studies, subjected to careful selection and further refinement for the most promising candidates.

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М. Кирпа, А. Захаров, В. Іванов. Оцінки методу TD-DFTB для широкомасштабного скринінгу органічних барвників.

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Досліджено ефективність напівемпіричного методу TD-DFTB (Time-Dependent Density Functional Tight Binding) у відтворенні спектральних властивостей органічних барвників на прикладі бібліотеки ізомерів тіофенвмісного донорно-акцепторного барвника Еффенбергера, відомого вираженою сольватохромією. Метою роботи було з'ясувати, наскільки придатним є прискорений підхід TD-DFTB для сучасних задач молекулярного дизайну, з необхідністю швидкої та надійної ідентифікації сполук з інтенсивними електронними переходами в довгохвильовій області УФ-Видимого спектру. Бібліотека містила 60 структур, в яких систематично варіювалися положення донорного (N,N-диметиламін) та акцепторного (NO_2) замісників, а також ступінь планарності π-каркаса. Для кожного ізомеру геометрія спочатку оптимізувалася на рівні DFTB, після чого енергії збудження розраховувалися за допомогою методу TD-DFTB. Отримані значення порівнювали з розрахунками TD-DFT (функціонали B3LYP та CAM-B3LYP), виконаними з геометріями, отриманими як методами DFT, так і DFTB. Така гібридна схема значно знижує обчислювальні витрати, дозволяючи проводити скринінг великих бібліотек без втрати точності. Наведено кореляцію між енергіями збудження, розрахованими за допомогою TD-DFTB та TD-DFT. TD-DFTB має тенденцію систематично занижувати енергії збудження, але значною мірою відображає сполуки з мінімальними енергіями збудження та високими силами осцилятора, що робить його надійним інструментом для початкового скринінгу. Було ідентифіковано кілька ізомерів з довгохвильовим поглинанням та достатньою інтенсивністю переходів, які є перспективними для подальшої модифікації. Таким чином, TD-DFTB у поєднанні з TD-DFT на оптимізованих геометріях DFTB демонструє оптимальний баланс між точністю та швидкістю попереднього скринінгу донорно-акцепторних барвників із заданими спектральними параметрами, що значно розширює можливості раціонального дизайну функціональних органічних матеріалів.

Ключові слова: *молекулярний скринінг, органічні барвники, TD-DFTB, TD-DFT, донорно-акцепторні системи, довгохвильове поглинання.*

Конфлікт інтересів: автори повідомляють про відсутність конфлікту інтересів.

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