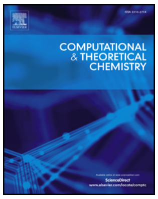
Computational and Theoretical Chemistry 1139 (2018) 90–101

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



Viewpoint article

Electronic structure and spectral properties of indole based fluorescent styryl dyes: Comprehensive study on linear and non-linear optical properties by DFT/TDDFT method

Dhanraj R. Mohbiya, Nagaiyan Sekar*

Department of Dyestuff Technology, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai 400 019, India

A R T I C L E I N F O

Keywords:
Vinyl indole
DFT
TD-DFT
GH
RSH

A B S T R A C T

The photophysics, linear and non-linear optical properties of indole based fluorescent styryl dyes are investigated with density functional theory and time-dependent density functional theory. The performance of seven global hybrid functionals - B3LYP, PBE0, BHHLYP, M06, M06-L, M06-2X, M06-HF and six range separated hybrid functionals - CAM-B3LYP, HISSbPBE, HSEH1PBE, ωB97, ωB97X, ωB97XD with poples [6-311 + + G(d,p)] and correlation consistence (cc-pVDZ, cc-pVTZ) basis sets is analyzed. The linear (vertical excitations, oscillator strengths) and non-linear optical parameters (first and second order hyperpolarizabilities) are calculated with each functional in combination with different basis sets for comparison. The vertical excitation of all the dyes are shown to have good correlation with the experimental values by the M06-2X/6-311 + + G(d,p) and HISSbPBE/cc-pVDZ combination with the least deviations (mean standard error) of 8.67 nm and 4.34 nm with respect to global and range separated hybrid functionals respectively. On the other hand, polarizability and hyperpolarizability values evaluated for all the dyes suggested that the dye which contain N-ethyl group as a donor and nitro group as an acceptor is found to have the largest NLO response as compared to other dyes. Mean standard error was calculated for each system with respect to global and range separated hybrid functionals to evaluate the accuracy of the DFT methods. Mean standard error of polarizability and hyperpolarizability obtained using global hybrids and range separated hybrid functionals are found to be basis sets dependent i.e. each functional and basis set combination perform differently.

1. Introduction

Density Functional Theory (DFT) and Time-Dependent (TD)-DFT turn out to be the important tools in predicting electronic properties of Donor-π-Acceptor (D-π-A) chromophoric systems [1–5]. In particular, DFT and TD-DFT are the quantum mechanical models which are mainly used to calculate the electronic properties of atoms and molecules in solutions using appropriate solvation models [6,7] as well as in condensed phases [8,9] in ground and excited states [10–15]. The choice of functional in DFT calculations is very important, because exact functionals for exchange and correlation are unknown, except for free electron gases [16]. Moreover, it is too naive to select functionals based on their chronological sequence. Hence, it is necessary to have Hartree-Fock (HF) exchange component in DFT hybrid functionals (e.g., B3LYP, BHHLYP, M06) to achieve the best computational build for a particular type of molecule [17].

The computational tools have become indispensable requirement for *a priori* evaluation of non-linear optical (NLO) properties of organic (principally D-π-A systems) and inorganic compounds [18–21]. Molecules with NLO properties are currently attracting considerable attention because of their potential applications in the optoelectronic devices in telecommunications [22], information storage [21], signal processing [23] and optical switching [24]. However, quantitative prediction of NLO properties is still a challenge because of the fact that the performance of functionals needs to be invariably benchmarked for a particular system [25–30]. Consequently, calculations of NLO properties using different DFT functionals have been an active area of research [31–34]. Moreover, the performance of functionals in predicting the NLO properties varies with the HF percent exchange (Table 1) in the global hybrid (GH) functionals [35]. The GH functionals that have a constant percentage of HF exchange became very popular as they perform well in electronic structure calculations [15,17,36]. Despite the vast popularity of GH functionals in the field of quantum chemistry calculations, there are shortcomings due to its exact HF exchange

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* Corresponding author.
E-mail address: n.sekar@ictmumbai.edu.in (N. Sekar).

https://doi.org/10.1016/j.comptc.2018.07.015
Received 18 April 2018; Received in revised form 23 July 2018; Accepted 23 July 2018

Table 1
HF exchange amount in GH and RSH functionals.

GH	HF%	RSH	HF%
B3LYP	20	CAM-B3LYP	19–65
PBE0	25	HISSbPBE	0–60–0
BHHLYP	50	HSEH1PBE	> 50
M06	27	ωB97	0–100
M06-L	0	ωB97X	15.77–100
M06-2X	54	ωB97XD	22.2–100
M06-HF	100	–	–

GH, Global hybrid.
RSH, Range separated hybrid.
HF%, percentage HF exchange amount.

amount for a range of molecules [37]. Consequently, to overcome the above crisis, range separated hybrid (RSH) functionals came into the picture. In this method, interelectronic Coulomb operator can be split into a short-range (SR) part and a long-range (LR) part [38,39].

$$\frac{1}{r_{12}} = \underbrace{\frac{\mathrm{erfc}(\omega r_{12})}{r_{12}}}_{\text{SR}} + \underbrace{\frac{\mathrm{erf}(\omega r_{12})}{r_{12}}}_{\text{LR}} \tag{1}$$

In recent years RSH functionals are extensively used for computing NLO properties [23,32,39]. The linear optical properties of chromophores carrying indole skeleton have been investigated [40]. So far, unsubstituted indole chromophore has been studied theoretically for its photophysics and photochemistry in aquatic microenvironment. Conte et al. [41] have presented the method to calculate the optical properties of indole in aqueous solution with the help of many-body perturbation theory combined with a quantum mechanics/molecular mechanics (QM/MM) approach. Later, Giussani et al. [42] studied the photophysical properties of indole skeleton after UV irradiation through the exploration of potential energy hyper surfaces of the singlet and triplet low-lying valence excited states with the help of CASPT2/CASSCF quantum chemical calculations. Consequently, DFT computation have been of importance in understanding the properties of indole derivatives [37,41–43]. Here, we have selected the simple indole based D-π-A derivatives with the different donor and acceptor substituents attached at the opposite end, and are studied for their linear and NLO properties in a solvent environment.

In this context, we report here benchmarking studies on the performance of GH and RSH functionals with different basis sets, in computing the NLO as well as electronic properties of indole-based D-π-A styryl dyes (Fig. 1). The geometries of indole styryl dyes (**1**–**6**) were optimized at the ground and excited state using B3LYP/6-311++G(d,p) level of theory. The linear and NLO properties obtained from GH functionals - B3LYP, PBE0, BHHLYP, M06, M06-L, M06-2X, M06-HF and RSH functionals - CAM-B3LYP, HISSbPBE, HSEH1PBE, ωB97, ωB97X, ωB97XD in combination with different basis sets, were compared with a view to benchmark the performance of these kinds of functionals. The structural modification of dyes **1**–**6** by introducing different electron donor and acceptor groups modulate their NLO response. The nitrogen atom present in indole unit acts as donor whereas cyano and nitro groups act as acceptors. This benchmarking study will also provide a comprehensive analysis of the effect of ethyl, −CN, and $-NO_2$ groups on electronic properties.

2. Computational methods

DFT and TD-DFT computations were performed on Gaussian 09 program [44] and the visualizations were done using Gauss view 5.0 [45]. All the computations were performed on HP workstation XW 8600 with Xeon processor, 4 GB RAM, and Windows Vista as the operating system. The ground state geometry of the dyes **1**–**6** were initially optimized using B3LYP functional with the basis set, 6-311++G(d,p) [43]. The B3LYP functional combines Becke's three parameter exchange functional (B3) [46] with the nonlocal correlation functional by Lee, Yang and Parr (LYP) [47]. Further all the linear and non-linear optical properties were evaluated by the each functionals in combination of different basis sets - 6-311++G(d,p), cc-pVDZ, cc-pVTZ. The geometry optimization of all the dyes in their ground state was carried out both in a vacuum and with the inclusion of solvent effects by using the polarizable continuum model (PCM) [48] as implemented in Gaussian 09. The vibrational frequencies of the optimized structures were computed using the same method to verify that the geometry corresponds to local minima on the potential energy surface. The vertical excitation energies at the ground state equilibrium were calculated with TD-DFT method [49]. The low-lying first singlet excited state (S_1) of each conformer was relaxed using the TD-DFT to obtain its minimum energy geometry. The performance of different DFT functionals in computing NLO properties was explored. The vertical excitation energy has been computed employing a wide panel of exchange-correlation (xc) functionals, including GH functionals - B3LYP, PBE0, BHHLYP, M06, M06-L, M06-2X, M06-HF, and RSH functionals - CAM-B3LYP, HISSbPBE, HSEH1PBE, ωB97, ωB97X, ωB97XD. The compositions of all the GH functionals and RSH functionals used here are given in Table 1.

3. Results and discussions

3.1. Ground state (S_0) and excited state (S_1) geometry

The optimized structure of dyes **1**–**6** were studied by means of DFT-B3LYP/6-311++G(d,p) level to evaluate the parameters such as bond length, bond angle, and torsion angle. The results of the torsion angle between indole and electron acceptor groups indicate that the dyes are almost planar in the S_0 state (Table S3). The results of bond length, bond angles and torsion angle in the S_0 and S_1 states for all the dyes are given in the Tables S2–4 and the subsequent optimized structures are depicted in the Figs. 2 and S1–5. Moreover, for all the dyes (**1**–**6**) the optimized geometry parameters were correlated with the experimental crystal X-ray structure for the S_0 state of tryptophan [50] where the

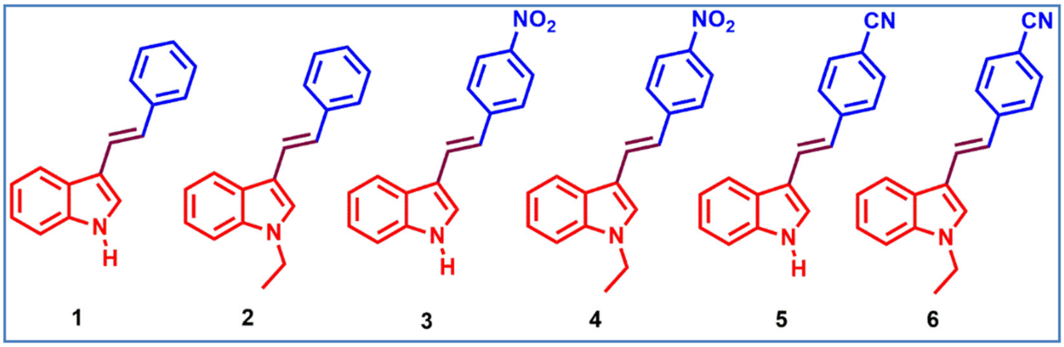

Fig. 1. Structures of the investigated dyes.