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A theoretical study on the ground and excited state behaviors of TTBC related carbocyanine dyes

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ABSTRACT

The effects of functional groups on the benzimidazole rings, length of the conjugated chain and alkyl groups bonded to the nitrogen atoms on the ground and excited state behaviors of the 1,1′,3,3′-tetraethyl-5,5′,6,6′-tetrachlorobenzimidazolocarbocyanine (TTBC or JC-1) have been analyzed via quantum chemical methods. DFT and TDDFT with B3LYP/6-31G(d,p) level of theory were used for the ground and excited state calculations, respectively. It has been found that TTBC has a very rigid geometry; no significant effect of functional groups has been predicted either as donor or acceptor on its optimum structure. However, the length of alkyl groups changes the structure of the molecule. It is possible to increase λ_{max} of TTBC based carbocyanine dye with NH_2, butyl/propyl and increasing polymethine chain length.

1. Introduction

In the last decades, interests in cyanine dyes [1] are rapidly increasing due to their wide application areas such as sensitizers in photographic industry [2], laser dyes [3,4], anti-tumor agent [5], non-linear optics [6], optical disk as recording media [7] and fluorescence probe for biological molecules [8].

Mitochondria is a very important organelle in many biological processes. The function of this organelle can be understood clearly by measuring mitochondrial membrane potential ($\Delta\Psi$). TTBC (JC-1) is one of the well-known molecular probe to monitor $\Delta\Psi$ which is used to detect a live or death cell [9,10]. The chemical structure of cationic TTBC dye is shown in Fig. 1. A high $\Delta\Psi$ (live) cause to form TTBC J-aggregate [11] and the cells fluoresce orange (590 nm) and at low $\Delta\Psi$ (death) TTBC stays in the monomeric form fluoresce green (527 nm) [12]. The big advantage of TTBC over rhodamines and other carbocyanines is that its color can be changed from green (monomeric form) to orange (aggregate form) depending on whether the cell alive or death [13]. Specific and selective cyanine dyes, which have a different range of absorption and emission wavelengths are very important to detect proteins, nucleic acids, other biological and non-biological materials [14]. So the synthesis of different selective cyanine dyes is under development.

The aim of this study is to examine the ground and excited state behaviors of the cyanine dyes; TTBC related compounds by using of quantum chemical methods. The effect of functional groups attached to benzene rings, the alkyl size bonded to nitrogens and the length of polymethine chain have been investigated to give an insight into new design of similar dyes as molecular labels in biochemical applications.

There are many theoretical studies which show that Time Dependent Density Functional Theory (TDDFT) [15–17] allow to simulate correctly UV–Vis spectra of organic dyes [18–24]. Although there are some disadvantages of TDDFT reported in the literature (charge transfer [25–27], double excitations [28–30] and Rydberg states [31,32]), it is demonstrated that these can be reduced by the adjustment of the functionals and the combinations of solvation models. Jacquemin and coworkers have been reported that TDDFT maximum absorption wavelengths agree excellently with the experimental ones for a number of dyes [33]. They also studied substitution effect on indigos, thioindigos and diazonium dyes [34–36]. Guillaumont and Nakamura showed that TDDFT correctly reproduces the UV/Vis spectrum of a series of organic dyes [37]. The substitution effect on the absorption spectrum of hemicyanine dyes with pyridine nucleus is studied by Wang et al. [38]. They showed that electron donor substituent increases maximum wavelength on the other hand *para* and *meta* substituted NO_2 decreases maximum wavelength relative to unsubstituted dye. Bertolino et al. investigated the solvent effect on a series of indocyanine dyes by TDDFT which are in good agreement with the experiments [39]. Very recently, Wang et al. reported a theoretical study on the excited state calculations of the dimethine cyanine dyes [40].

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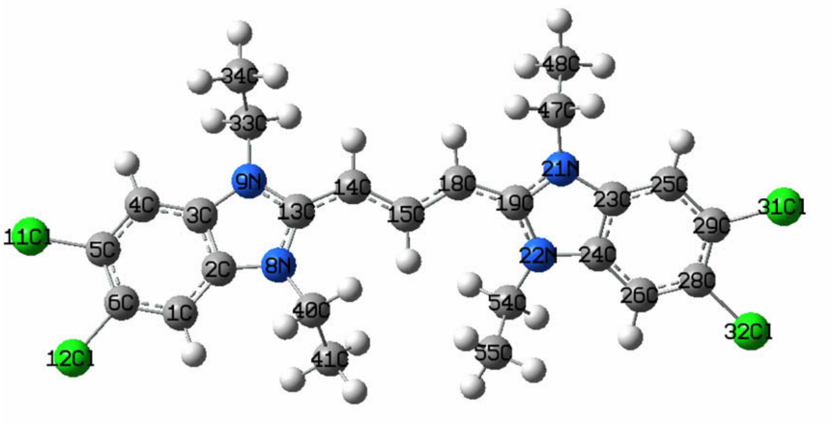

Fig. 1. Cationic structure of TTBC.

2. Methodology

All computations have been carried out with Gaussian 03 [41] program. The Density Functional Theory was carried out in the optimization part with the Becke Three Parameter Lee, Yang and Parr B3LYP [42] functional by using 6-31G(d,p) basis set. The frequencies were checked for imaginary eigenvalues to ensure that the optimized structures are energy minimums. Time Dependent Density Functional Theory (TDDFT) has been used for the excited state calculations on the ground state structures. The first 15 vertical singlet excited states were computed by using TDDFT/B3LYP/6-31G(d,p) on the optimized geometries. The iodide ion (counter ion) of the TTBC has been ignored in all calculations. The overall charge of the molecule is (+1).

3. Results

3.1. Optimization part of TTBC

The calculated and experimental geometrical parameters are given in Table 1. We have carried out a linear regression analysis to compare optimized structure with the X-ray structure [43], the correlation coefficient was found as 0.9894 for bond lengths and 0.9813 for bond angles. The mean absolute error is 0.0115 and 0.7728 for the bond lengths and angles, respectively. The maximum percent relative error is 3.10 for the bond length at C40–C41 and 3.35 for C48–C47–N21 bond angle. These atoms are in the ethyl groups. B3LYP/6-31G** level of theory overestimates the C40–C41 bond length by 0.046 and C48–C47–N21 bond angle by 3.67 and the largest discrepancies between X-ray and computed structure are seen in the ethyl moieties. Ethyl groups bonded to N9 and N22 atoms are in up position while the other two ethyls bonded to N8 and N21 atoms are in down position from the molecular plane (Fig. 1). However, in the X-ray structure ethyls in N8, N9 are in up and in N21, N22 are in down position. We have performed optimizations by changing the orientations of the ethyl groups. It was observed that, these groups can easily rotate with almost no significant energy change.

Table 1
Some selected bond lengths and angles of TTBC.

Bond lengths (Å)			Bond angles (°)		
Atoms	DFT	X-ray	Atoms	DFT	X-ray
C(1)–C(2)	1.3894	1.3747	N(8)–C(2)–C(1)	131.4	131.2
C(2)–C(3)	1.4007	1.3840	N(9)–C(33)–C(34)	113.1	109.5
C(3)–C(4)	1.3899	1.3914	N(9)–C(13)–N(8)	107.1	107.2
C(4)–C(5)	1.3980	1.3796	N(9)–C(3)–C(4)	131.7	131.0
C(5)–C(6)	1.4115	1.3876	Cl(11)–C(5)–C(6)	121.0	119.5
C(6)–C(1)	1.3982	1.3846	Cl(11)–C(5)–C(4)	118.0	118.2
C(5)–Cl(11)	1.7392	1.7383	C(15)–C(18)–C(19)	129.9	129.1
C(6)–Cl(12)	1.7396	1.7293	C(15)–C(14)–C(13)	129.9	129.6
C(2)–N(8)	1.3956	1.3927	C(14)–C(13)–N(8)	130.2	130.8
N(8)–C(13)	1.3764	1.3635	N(8)–C(13)–C(14)–C(15)	19.6	5.1
N(9)–C(13)	1.3777	1.3717			
N(9)–C(3)	1.3909	1.3886			
N(9)–C(33)	1.4674	1.4567			
N(8)–C(40)	1.4651	1.4634			
C(13)–C(14)	1.4093	1.3944			
C(14)–C(15)	1.3957	1.3797			

The bond lengths along the backbone are about 1.400 Å which is in between single and double bonds of carbon that reflects the conjugation on the molecular plane. The size of the TTBC is about 17.5 Å × 8.8 Å (X-ray length = 17.4 Å × 8.1 Å) and the deviation from the planarity is 19.6°. Although the bond lengths are in good agreement with the experiment the dihedral angle differ by 15 ° which might be due to the crystal packing effect. These results reveal that B3LYP/6-31G** level of theory is suitable for the description of the geometric structure of TTBC without sacrificing much accuracy.

NBO (Natural Bond Orbital) and Mulliken charges were used for the charge analysis. The molecule was divided into seven charge groups. These groups are shown in Fig. 2a by circles with group numbers. The groups are four alkyls (1,3,4,6), two benzimidazoles (2,5) and one polymethine chain (7). The charges of these groups are shown in Fig. 2, where the charge of each atom is visualized in color scale. The color scale changes from red (most negative) to green (most positive). The most negative atoms are nitrogens while their carbon neighbors bonded to polymethine chain hold the most positive charge. The alkyl groups are carrying all positive charges while polymethine chain is negatively charged and the benzimidazole rings have almost zero charge according to both Mulliken and NBO charge analysis. But the magnitudes of the charges are different in each method. Alkyl groups have similar charges in both methods however the charge on polymethine chain is almost doubled in NBO method.

The HOMO–LUMO shapes are given in Fig. 3. There is no electron distribution on the ethyl groups and the electrons spreads out on the backbone of the molecule. The HOMO–LUMO pictures show that the electrons are migrated from Cl atoms to the molecule. Chlorine atoms act as electron donor.

3.2. Side group effects on the TTBC

The quantum mechanical calculations can play an important role to design new versatile functional dyes with tuned optical and spectral properties. In this part, the ground and excited state