



Theoretical study on photochemical behavior of *trans*-2-[4'-(dimethylamino)styryl]benzothiazole

Francis A.S. Chipem, Soumya Chatterjee, G. Krishnamoorthy*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India

ARTICLE INFO

Article history:

Received 4 February 2010

Accepted 16 June 2010

Available online 23 June 2010

Keywords:

TICT

TDDFT

Photophysics

Photoisomerization

Push–pull aromatic olefin

ABSTRACT

Photochemistry of *trans*-2-[4'-(dimethylamino)styryl]benzothiazole (*t*-DMASBT) has been examined theoretically. Ground state calculations are performed by density functional theory (DFT) method. For excited-state calculations restricted configuration interaction singles (RCIS) combined with time dependent DFT (TDDFT) approach was used. Theoretical calculations predicted the existence of two ground state conformers and the photophysics of both the conformers are nearly identical. With torsional rotation of dimethylamino group, the energies of S_1 and S_2 states increase, but that of S_3 state decreases. In contrary to an earlier report [J. Photochem. Photobiol. A: Chem. 195 (2008) 368–377], the calculation predicted at the perpendicular geometry the HOMO is localized on dimethylamino and, HOMO and LUMO are decoupled. Excitation from HOMO to LUMO at perpendicular geometry results in twisted intramolecular charge transfer (TICT) state. Avoided crossing of S_3 and S_1 states causes a barrier for formation of TICT state from locally excited state. Potential energy surface of isomerization constructed by TDDFT method suggests that the photoisomers are formed through phantom state in a nonradiative way, not by a radiative way from *cis* and *trans* isomers as proposed earlier by Saha et al. [J. Photochem. Photobiol. A: Chem. 199 (2008) 179–187].

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1. Introduction

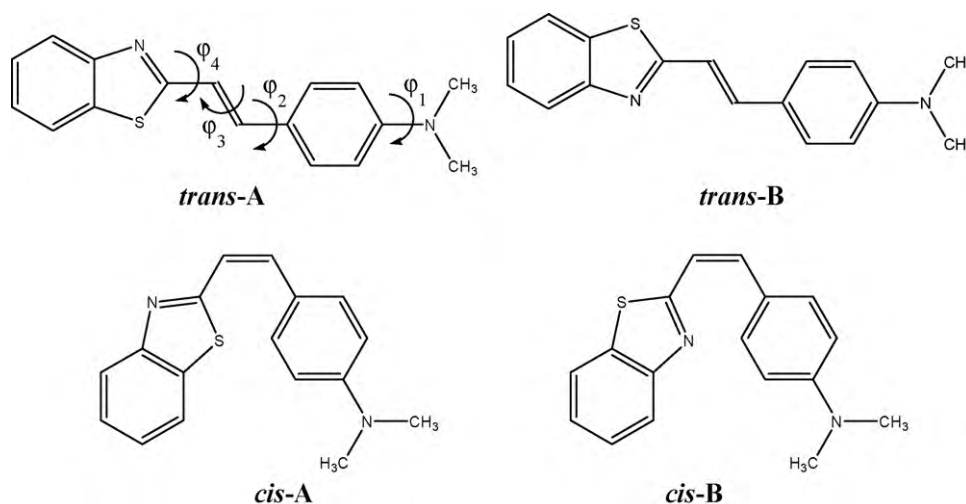
Excited-state torsional motion about carbon–carbon double bond that leads to *trans*–*cis* photoisomerization is an important nonradiative decay channel for many π -systems [1,2]. The photoisomerization has been known for several decades to dominate the photochemistry of aromatic olefins, and has been studied extensively and reviewed [1–5]. ‘Push–pull’ aromatic olefins are much more interesting [6–12]. The presence of single bonds linking electron donor and electron acceptor groups in ‘push–pull’ systems may allow twisted intramolecular charge transfer (TICT) state formation. On the other hand, the double bonds can also lead to *trans*–*cis* isomerization which can compete with TICT state formation.

trans-2-[4'-(Dimethylamino)styryl]benzothiazole (*t*-DMASBT) is a push–pull aromatic olefins, which has benzothiazole ring on one side of the olefin bond and dimethylanilino ring on the other side (Scheme 1). Fayed and Ali were the first to synthesize and study the photophysics of *t*-DMASBT [13]. They suggested that *t*-DMASBT is emitting from the intramolecular charge transfer (ICT) state and is due to increase in dipole moment in the S_1 state. Saha et al. had elaborated utility of *t*-DMASBT. It was found that the fluorophore can

be used as molecular probe to study biological functions as well as biomimicking systems [14]. *t*-DMASBT can act as a surface probe to monitor the premicellar aggregation and the phase change during the process [15] and also it induces the formation of nanotubular suprastructures by cyclodextrins [16–18]. Saha et al. also reinvestigated DMASBT both experimentally and theoretically and proposed that DMASBT emits from TICT state in polar solvents [19]. They hypothesized that the S_3 state of the molecule developed a high dipole moment with twisting of dimethylamino group and thereby got stabilized in polar solvent to emit TICT fluorescence in polar solvents. But there is large overlap between the HOMO and LUMO (reported by Saha et al.) that involved in the formation of TICT state. However it is known [20,21] that under charge transfer conditions the donor and the acceptor are orbitally decoupled and therefore there is little or no overlap between the atomic orbitals contributing to the HOMO and those to the LUMO [12,22–24]. In addition the HOMO that is supposed to localize on the electron donating dimethylamino, is localized on the other parts of the molecules in the HOMO obtained by Saha et al. [19]. These behaviors of HOMO and LUMO in the formation of TICT state are unexpected. Saha et al. [14] also studied the photoisomerization of DMASBT and reported that the photoisomerization of DMASBT is different from that of stilbene and other olefins. According to their model the *cis*–*trans* isomerization occurs thermally in the first excited state and both the isomers relax to the ground state by radiative way. However

* Corresponding author. Tel.: +91 361 2582315; fax: +91 361 2582349.

E-mail address: gkrishna@iitg.ernet.in (G. Krishnamoorthy).



Scheme 1. Different molecular forms of DMASBT.

photoisomerization via phantom singlet state, $^1p^*$ was reported even in cases of many donor and acceptor substituted stilbenes [6–12].

Thus we reinvestigated theoretically the excited-state properties of DMASBT by time dependent density functional theory (TDDFT) to verify Saha et al. model about TICT emission and photoisomerization in DMASBT. Our theoretical calculations clearly suggest that HOMO is more localized on the donor dimethylamino group and the LUMO is localized on the rest of the molecule and there is a minimum overlap between these molecular orbitals. In addition the calculations predict that there is avoided crossing between the S_3 and S_1 states that makes a barrier for the formation of TICT state. In contrary to Saha et al. model the photoisomerization of DMASBT is also predicted to occur via perpendicular geometry in a nonradiative way.

2. Computational method

The molecular geometries in the ground state were obtained by full optimization of structural parameters employing Berny optimization algorithm by density functional calculation in spin restricted shell wavefunction manner [25,26]. The functional used in the calculation was B3LYP where the gradient corrected exchange functional of Becke [27] and the correlation functional of Lee, Yang and Paar (LYP) [28] were employed. The basis set used in all the calculations was 6-31G(d,p) which includes polarization functions, d orbitals for C, N, O and S atoms and p orbitals for H atoms.

Configuration interaction singles (CIS) [22,29] and complete active space self-consistent field (CASSCF) [30–32] methods are very popular computational methods for the excited-state electronic structures. CIS method is less expensive and found to overestimate the energies [33,34]. CASSCF method is also known to over estimate the excitation energy to ionic-type or charge transfer and it is necessary to include dynamic correlation to correct this behavior [32,35]. CASSCF are good for small systems, but quite expensive for large systems [30,31,36]. The geometries obtained at the CIS level as well as molecular properties are quite reasonable and correct, at least as a first approximation for a variety of molecules [34,37,38], including 4-dimethylaminobenzonitrile [39]. TDDFT calculations were also used successfully to explain the formation of the TICT state in systems like Michler's ketone and dimethylamino fluorenone [23,40]. In view of this we have performed ab initio CIS calculation to obtain the molecular geometry. As the energy predicted by the calculations are quite high com-

pared to experimental values, using the CIS optimized geometries as input TDDFT calculations were employed to obtain the energies.

Vertical excitation energy calculations were performed on the optimized ground and excited S_1 state geometries for the assignment of excitation and emission energies, respectively, by TDDFT/B3LYP/6-31G(d,p) [41,42]. All the computations were performed with a developed version of Gaussian 03W [43].

3. Results and discussion

3.1. Conformers

Two conformers are possible for *t*-DMASBT (Scheme 1) and optimized geometrical parameters for both the conformers are compiled in Table 1. *Trans-A* is the most stable form of the molecule. However the energy difference between the two *trans* conformers is negligible, and DFT calculations predict a rotational barrier of 0.34 eV for the conversion of one conformer to other conformer (Fig. 1). Comparison of data in Table 1 shows that the geometrical parameters and properties of both the conformers are nearly same. The molecule is almost planar with small dihedral angle ($\sim 5^\circ$) between the dimethylamino group and rest of the molecule. The excitation energies were obtained by the vertical transition of the ground state geometries. The difference in excitation energies of both the conformer is very small and values obtained by TDDFT calculation are in excellent agreement with experimental value (Table 1). The longest wavelength transition is intense and has contribution only from HOMO–LUMO excitation and the transition is

Table 1
Optimized Parameters for *trans*-DMASBT in S_0 and S_1 states.

Parameters	<i>trans-A</i>		<i>trans-B</i>	
	S_0	S_1	S_0	S_1
Energy (eV) ^a	0.0	3.2229	0.0009	3.2268
T.E. ^b (nm)	384 (384)	419 (447)	383	419
Oscillator strength (<i>f</i>)	1.3051	1.4833	1.3607	1.4881
μ (D)	5.2		5.1	
Dihedral angles ($^\circ$)				
φ_1	5.0	0.0	4.9	0.1
φ_2	180.0	180.0	180.0	180.0
φ_3	180.0	180.0	180.0	180.0
φ_4	180.0	180.0	0.0	0.0

^a With respect to ground state energy of *trans-A*.

^b T.E.: transition energy and the values in parentheses are experimental value for *t*-DMAPBT in cyclohexane from Ref. [19].

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