

Research Notes

Photoisomerization of *trans*-2-[4'-(Dimethylamino)styryl]benzothiazole

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ABSTRACT

Photoreaction of *trans*-2-[4'-(dimethylamino)styryl]benzothiazole (*t*-DMASBT) under direct irradiation has been investigated in dioxane, chloroform, methanol and glycerol to understand the mechanism of photoisomerization. Contrary to an earlier report, isomerization takes place in all these solvents including glycerol. The results show that restriction on photoisomerization leads to the increase in fluorescence quantum yield in glycerol. The results are consistent with the theoretically simulated potential energy surface reported earlier using time-dependent density functional theory (TDDFT) calculations. DFT calculations on *cis* isomers under isolated condition have suggested that *cis*-B conformer is more stable than *cis*-A conformer due to hydrogen-bonding interaction. In the ground state, *cis*-DMASBT is predominantly present as *cis*-B. The fluorescence spectra of the irradiated *t*-DMASBT suggested that photoisomerization follows not the adiabatic path as proposed by Saha *et al.*, but the nonadiabatic path.

INTRODUCTION

Due to wide applications, fluorescing donor–acceptor substituted push–pull styryl dyes have received considerable attention (1–5). *trans*-2-[4'-(Dimethylamino)styryl]benzothiazole (*t*-DMASBT, Chart 1) is an interesting push–pull styryl dye, and was suggested as a good microsensor to study the biological functions as well as biomimicking systems (6). Fayed *et al.* showed that *t*-DMASBT emits from an intramolecular charge transfer (ICT) state in polar solvents (7). Later Saha *et al.* (8) studied the spectral characteristics of *t*-DMASBT and suggested that it emits from the twisted ICT (TICT) state in polar solvents. They also proposed that the polarity of the S₃ state increases by torsional rotation of the dimethylamino group and at 90° it forms the TICT state. In the gas phase, the energy of the TICT state is higher than that of the planar S₁ state, but polar solvents stabilize the TICT state and make it as the emitting state. However, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) reported by them for the twisted geometry are not consistent with the formation of a charge transfer state. There was a large overlap between the HOMO and LUMO and in the HOMO the electron density that is supposed

to be localized on the dimethylamino group (donor) is localized on the other part of the molecule. Thus, we reinvestigated the photochemical nature of *t*-DMASBT theoretically (9). Our calculations predicted that *t*-DMASBT is present in two conformeric forms, *trans*-A and -B (Fig. 1). Their relative populations and spectral characteristics and nature of the excited states are predicted to be nearly the same. Our calculations also suggested that twisting of the dimethylamino group is energetically favored compared with twisting of dimethylanilino or dimethylanilino-styryl moieties. With torsional rotation of the dimethylamino group, the energy of the S₃ state decreases and those of the lower energy states increase. The S₃ state crosses the S₂ state, but there is an avoided crossing between S₃ and S₁ states. At the perpendicular geometry, the emitting state is described by HOMO–LUMO excitation. The HOMO and LUMO are decoupled with the HOMO localized on the donor dimethylamino group and the LUMO localized on the other part of the molecule. Thus, the donor lone pair becomes available for charge transfer to the decoupled LUMO that results in the formation of the TICT state.

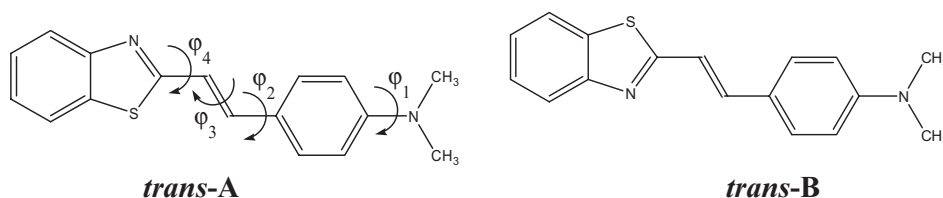
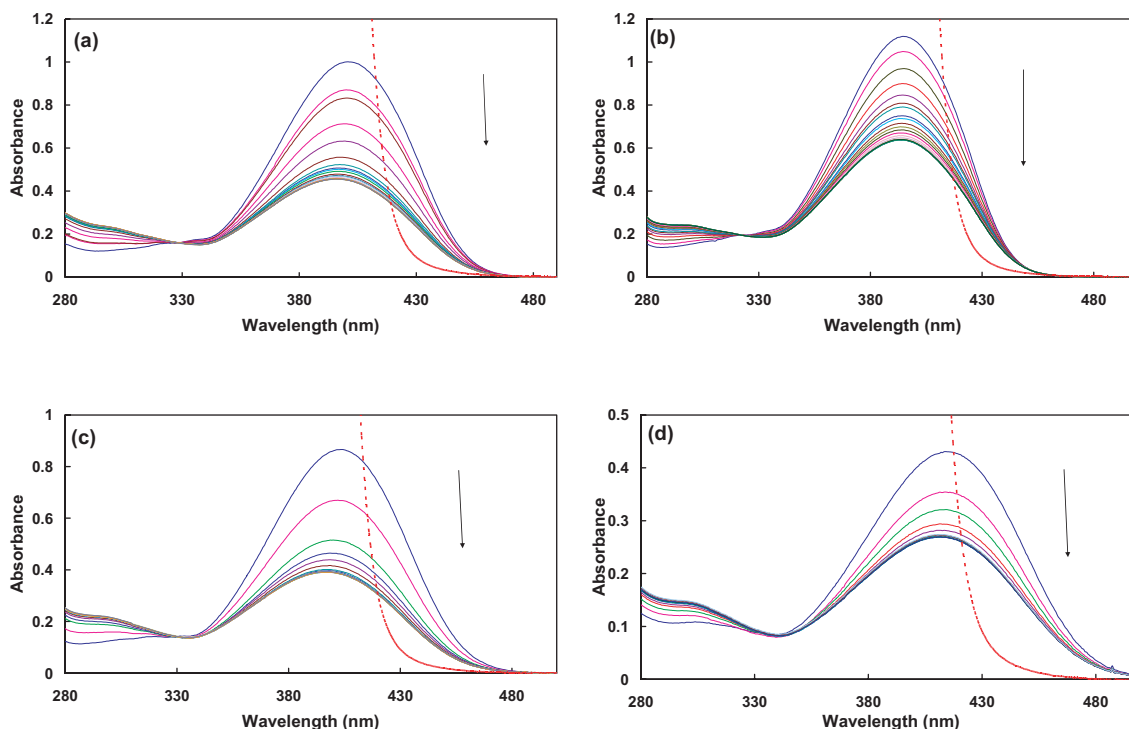
t-DMASBT has been shown to act as an excellent sensor for a variety of heterogeneous systems (10–16). It was used as a surface probe to monitor the pre-micellar aggregation in sodium dodecyl-sulfate, cetyltrimethyl ammonium bromide and Triton X 100 (10) and brij's (11). It was also found that *t*-DMASBT induces the formation of cyclodextrin nanotubular suprastructures (12–14). Recently, Purkayastha *et al.* used *t*-DMASBT as a fluorophore to demonstrate the targeted drug delivery of nanoparticle (15). They also utilized *t*-DMASBT to study the ionic surfactant created peripheral confined water around silver nanoparticle (16). Despite the fact that the sensitivity of the photophysics and photochemistry of *t*-DMASBT to environment is responsible for its wide application in various systems, the mechanism of nonradiative decay and photoisomerism are still controversial.

Saha *et al.* (6) investigated the effect of temperature on the fluorescence spectral characteristics of *t*-DMASBT. They hypothesized that in a highly viscous polar medium, the restricted rotation of the dimethylamino group causes a greater extent of donation of charge toward acceptor, thereby stabilizing the TICT state and the temperature-induced TICT fluorescence quenching is observed without any isomerization. However, in low polarity solvents the decrease in fluorescence was attributed to the temperature-dependent *cis*–*trans* isomerization. According to Saha *et al.*, the isomerization is supposed to take place in the excited state *i.e.* by adiabatic process and the so formed *cis* isomer

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Chart 1. Structures of different conformers of *t*-DMASBT.**Figure 1.** UV-Visible spectra of *t*-DMASBT at different irradiation times (using 420 nm cutoff filter) in (a) chloroform (b) dioxane (c) methanol and (d) glycerol (dotted line shows the spectrum of the 420 nm cutoff filter).

should relax radiatively. On the other hand, our time-dependent density functional theory (TDDFT) calculations predicted that the photoisomerization of *t*-DMASBT occurs *via* a phantom state which decays to *cis* and *trans* isomers nonradiatively (9). Therefore, we have investigated the photochemistry of *t*-DMASBT in different solvents. The main objectives are to determine whether (1) *t*-DMASBT isomerizes in polar viscous media such as glycerol or not and (2) the isomerization follows the adiabatic or nonadiabatic path.

MATERIALS AND METHODS

t-DMASBT was synthesized by following the procedure reported by Fayed *et al.* (7). A solution of *p*-dimethylaminobenzaldehyde (0.002 mmol) in dry dimethyl formamide (DMF) (4 mL) was added dropwise to a solution of 2-methylbenzothiazole (0.003 mmol) and powdered KOH (0.02 mmol) in 8 mL of dry DMF with continuous stirring. The mixture was stirred at 140°C. After 48 h the mixture was cooled to room temperature and dilute HCl (10%) was added to it to make it weakly acidic. The compound was extracted with dichloromethane. The compound was purified first by column chromatography and further by preparative thin layer chromatography using a hexane–ethyl acetate mixture.

Dioxane, chloroform, methanol all HPLC grade and glycerol AR grade were used as received. CDCl_3 was used for NMR experiments. *p*-dimethylaminobenzaldehyde, 2-methylbenzothiazole and CDCl_3 were

procured from Sigma–Aldrich. All other solvents were procured from Rankem, India and were tested for spurious absorbance/fluorescence in the region of spectral measurements. Irradiations were carried out in a standard quartz cell/NMR tube at room temperature in presence of air with light from a 350 W ozone free Xe-arc lamp. In addition to water filter, Scotch cutoff filters were used when required. For irradiation experiments, the concentrations of the solutions were 3×10^{-5} to 5×10^{-5} M (in 1 cm quartz cell) and 10^{-2} M (in NMR tube). For fluorescence measurement, the absorbance of the solutions was kept below 0.1 at the wavelength of excitation. The irradiation of the solutions in quartz cells and NMR tube were followed by UV-Visible absorption and NMR spectrometers respectively. UV-Visible absorption and fluorescence spectra were recorded on a Varian Cary 100 spectrometer (Varian Australia Pty Ltd, Palo Alto, Australia) and Jobin-Yvon Spex Fluoromax 4 fluorometer (Horiba Instruments Incorporated, Edison, NJ, USA) respectively. ^1H NMR was recorded using a 400 MHz Varian instrument (Varian Mercury plus, Palo Alto, CA, USA).

All the calculations were carried out using the GAUSSIAN 03 program (17). The ground state geometries were obtained by full optimization of structural parameters using DFT employing the 6-31G(d,p) basis set using spin-restricted shell wavefunctions (18,19). Geometry optimizations were carried out using Becke's three-parameter hybrid functional B3, (20) with nonlocal correlation of Lee-Yang-Parr, LYP (21), abbreviated as B3LYP. The minimum energy nature of the stationary points was verified from vibrational frequency analysis. The excitation energies were obtained by vertical excitations of optimized ground states using TDDFT/B3LYP/6-31G(d,p) calculations (22,23).

RESULTS AND DISCUSSION

t-DMASBT was irradiated in chloroform using a 420 nm cutoff filter and the reaction was monitored with a UV–Visible absorption spectrometer (Fig. 1a). Upon irradiation, the 400 nm absorption band of *t*-DMASBT gradually blue shifted with a hypochromic effect. The photostationary state was reached in 35 s of irradiation and an isosbestic point was observed at 327 nm. The isosbestic point revealed a simple one-to-one conversion of *t*-DMASBT to *cis* product. To confirm the formation of *cis* isomer further, we followed the reaction by ^1H NMR in

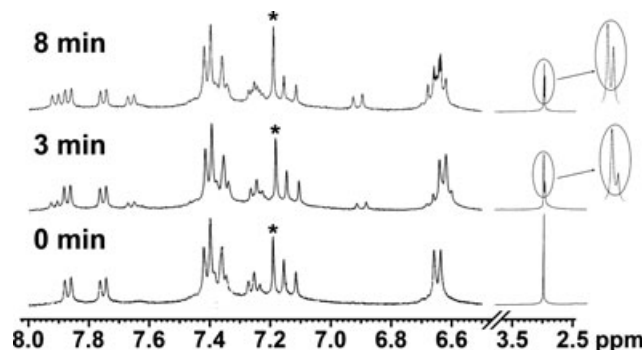


Figure 2. ^1H NMR spectra of *t*-DMASBT in CDCl_3 at different irradiation times (using 420 nm cutoff filter; the intensity of the peaks is expanded in the aromatic region for clarity, * denotes chloroform peak).

CDCl_3 . Figure 2 shows the NMR spectra of *t*-DMASBT at different irradiation times. One of the signals corresponding to a *trans* olefinic proton of *t*-DMASBT overlaps those of the aromatic protons, but the other olefinic proton appears as a doublet with a coupling constant of 16.0 Hz at δ 7.14 ppm. This olefinic proton was used to monitor the reaction. Upon irradiation, the intensity of the doublet at δ 7.14 decreases, and an olefinic proton of *cis* isomer appears at δ 6.91 (d, J = 12.0 Hz, 1H). Other peaks corresponding to the *cis* isomer also emerge. This confirms that the blueshifted photoproduct obtained is the *cis* isomer of DMASBT. Figure 1 also shows the irradiation in nonviscous solvents dioxane (non polar) and methanol (polar) and also in a viscous polar solvent glycerol. In all the solvents, formation of *cis* isomer is observed as in chloroform. Without determining the spectrum of the *cis* isomer, it is difficult to predict the effect of solvent on the photostationary state. However, comparison of the panels in Fig. 1 suggests higher *trans* contents in dioxane and glycerol. These changes may be real or may be due to spectral shifts that change the incident light excitation-ratio of the two isomers. The absorbance ratio of the sample after irradiation (*i.e.* the photostationary state) and before irradiation (*i.e.* the *trans* isomer) at absorption maxima, $A_{\text{ai}}/A_{\text{bi}}$ was calculated. $A_{\text{ai}}/A_{\text{bi}}$ ratio follows the order methanol (0.43) < chloroform (0.44) < dioxane (0.53) < glycerol (0.67). However, the absorption maxima of the *trans* isomers follows the order dioxane (394 nm) < chloroform (400 nm) < methanol (402 nm) < glycerol (416 nm). Therefore, it may be inferred that the content of *trans* is larger in dioxane and glycerol at photostationary state due to solvent effect.

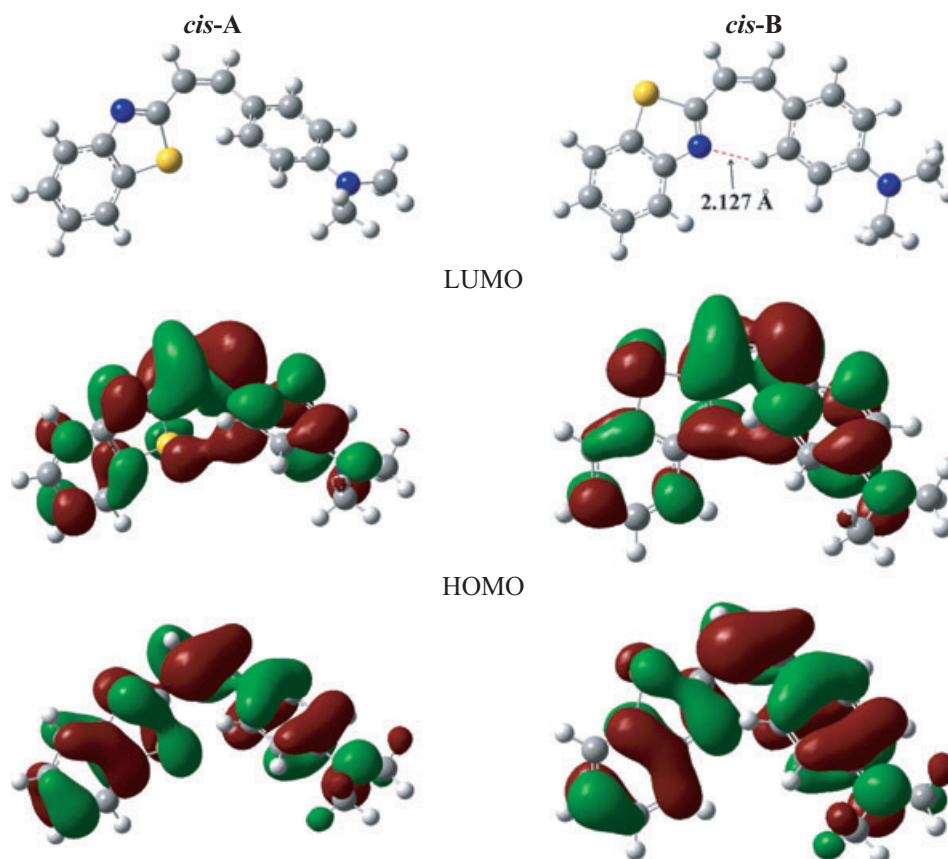


Figure 3. Optimized structures along with HOMO and LUMO of *cis*-A and -B.

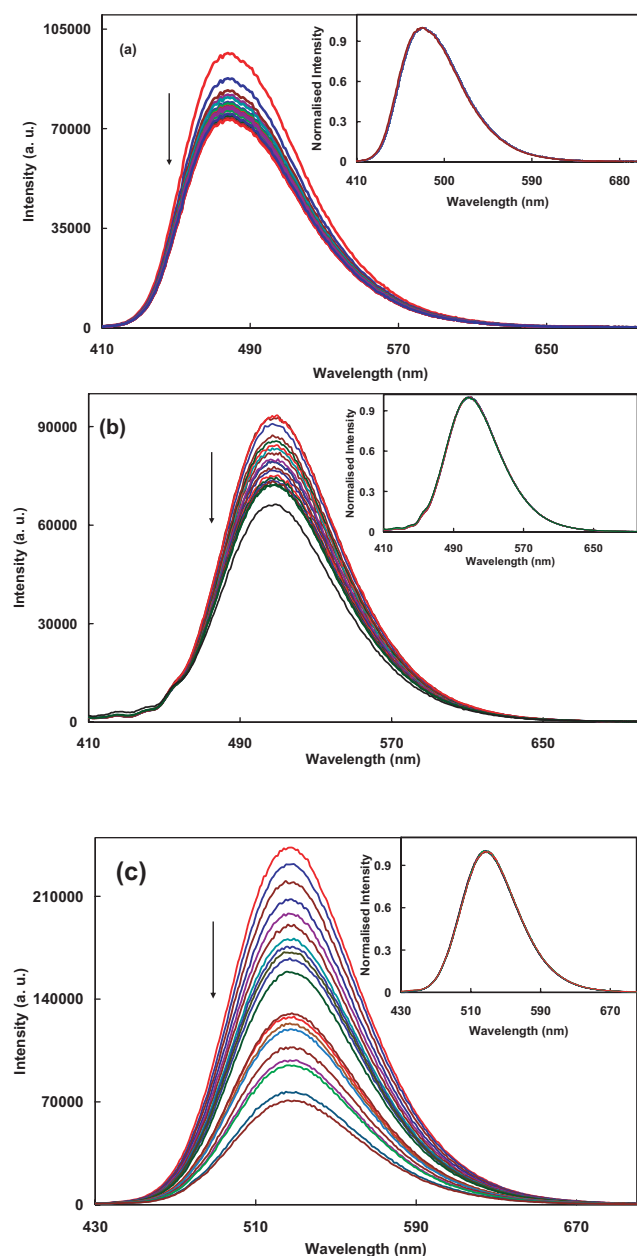


Figure 4. Fluorescence spectra of *t*-DMASBT in (a) dioxane, (b) acetonitrile and (c) glycerol (inserts show the normalized spectra) in the course of the irradiation time (all irradiations are carried out in fluorescence instrument with $\lambda_{\text{exc}} = 395$ nm and 10 nm slit width).

Saha *et al.* (6) hypothesized that in a highly viscous medium such as glycerol the restricted rotation of the dimethylamino group causes a greater extent of donation of charge toward the acceptor thereby stabilizing the TICT state responsible for the large Stokes shift in the fluorescence. Only in low polarity solvents, where TICT emission is very weak, the molecule undergoes a temperature-dependent photoisomerization. The temperature-induced TICT quenching occurs in a polar viscous medium without any isomerization. But our studies clearly establish that *t*-DMASBT photoisomerizes in all the media including glycerol. The molecule is predicted to have planar geometry in the ground state by both our DFT calculations (9) as well as by AM1 calculations (6,8). The corresponding Franck–Condon state

Table 1. Optimized geometrical parameters for *cis*-conformers in the ground state.

Parameters	<i>cis</i> -A	<i>cis</i> -B
Relative Energy [†] (kcal mol ^{−1})	6.75	3.77
Transition energy (nm)	392	394
Oscillator strength	0.5477	0.8420
Dipole moment (<i>D</i>)	4.8	3.8
Dihedral angle [‡] (°)		
Φ_1	9.4	0.0
Φ_2	174.4	0.0
Φ_3	38.2	0.1
Φ_4	7.4	5.2

[†]With respect to ground state energy of *trans*-A.

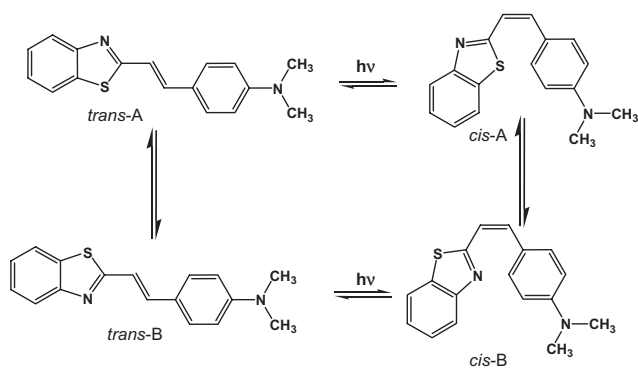
[‡]Dihedral angles defined in Chart 1.

has to have planar geometry and the molecule has to relax from the planar Franck–Condon state to the TICT state. Therefore, any restriction on rotational motion is expected to hinder not only the reverse process but also the formation of the TICT state. Therefore, the enhancement in fluorescence quantum yield of *t*-DMASBT in glycerol is due to restriction on twisting of the olefinic double bond that leads to isomerization.

In *t*-DMASBT, the TICT state is formed by the rotation of the smaller dimethylamino group, but the competing torsional rotation around the olefinic double bond involves the rotation of dimethylanilino group or the benzothiazole group. Fluorescence quantum yields of *trans*-stilbene were also shown to be temperature and viscosity dependent due to the twisting motion about the central bond of phenyl ring (24–33). Although the fluorescence quantum yield decreases with increase in temperature, it increases with increase in viscosity. The observed marked increase in fluorescence quantum yield of *trans*-stilbene in glycerol on lowering of temperature was attributed to the fact that the processes of fluorescence and isomerization are coupled with changing temperature in highly viscous solvents (26–28). It was also reported that the normally very weakly fluorescent *cis*-stilbenes (29–31) and the weakly fluorescent *trans*-stilbenes become strongly fluorescent in highly viscous media (32). Our present results on *t*-DMASBT also indicate that photoisomerization competes with fluorescence.

As reported earlier (9), *t*-DMASBT is present in two conformeric forms, *trans*-A ($\mu = 5.2$ D) and *trans*-B ($\mu = 5.1$ D). The energy difference between the two conformers is only 0.2 kcal mol^{−1} and thus both conformers are predicted to be equally probable. As the difference in dipole moments between the two conformers is negligible their relative population is nearly the same in all the media. Such conformers equilibrate in the ground state, but not in the excited state (34). Consequently, the presence of the two conformers may be reflected in λ_{exc} dependence fluorescence spectra (35). The shifts in the fluorescence spectra with λ_{exc} are very small (see Supporting information). It should be noted that the molecular parameters predicted by the theoretical calculations for both the conformers are nearly identical and the emission energies predicted are the same (9).

trans-A and -B conformers upon one bond twist give *cis*-A and -B conformers, respectively (Scheme 1). Unlike organic glasses or other restricted media, the flexibility of the media in our reaction conditions should allow thermal equilibration in all these environments. The absorption spectra were recorded after such equilibration between the conformers. As the molecular



Scheme 1. Photoisomerization of *t*-DMASBT.

parameters of *trans* conformers were already reported (9), we calculated the molecular parameters of *cis* conformers under isolated condition and the optimized structures are shown in Fig. 3 and the data are compiled in Table 1. The calculations predict that *cis*-B is more stable than *cis*-A by 0.1295 eV (*ca* 3 kcal mol⁻¹). Although the *trans* isomer is present as both A and B conformers, the *cis* isomer is predominantly present in the B form and the population of *cis*-A is less than 1%, even in the most polar environment. *cis*-B is more stabilized by the presence of pseudohydrogen bonding between thiazole nitrogen and one of the phenyl hydrogen (Fig. 3). The presence of hydrogen bond in *cis*-B also planarizes the molecule (Table 1). In protic solvents such as methanol and glycerol, this hydrogen bond may break to form intermolecular hydrogen bond. However, the transition energies of both conformers are nearly same and are described by excitation of an electron from highest occupied molecular orbital to lowest unoccupied orbital in both conformers. The smaller oscillator strengths of the *cis* conformers (Table 1) compared to those of the *trans* conformers (oscillator strength *ca* 1.3; 9) explain the observed hypochromic effect of the absorption spectra on photoisomerization.

Thus, the *ca* 23-fold increase in fluorescence quantum yield of *t*-DMASBT in glycerol observed by Saha *et al.* may be attributed to fact that the viscous medium enhanced the torsional barrier leading to photoisomerization. Saha *et al.* also reported that the fluorescence quantum yield of *t*-DMASBT decreases with increase in temperature in both dioxane and glycerol (6). Our earlier theoretical calculations (9) had predicted a small barrier for twisting in the first excited state of *t*-DMASBT to attain a perpendicular geometry. Therefore, the thermally activated non-radiative de-excitation process that competes with fluorescence may be assigned to isomerization.

The potential energy surface constructed by Saha *et al.* has a huge barrier for rotation (77 kcal) in the ground state and it is also considerable (36 kcal) in the excited state without a phantom state (6). Although their potential energy surface predict no photoisomerism, they hypothesized that the *trans* isomer (*t**) undergoes torsional rotation in the first excited state to form *cis* isomer (*c**) in the excited state and that the *cis* isomer relaxes radiatively. Contrary to the adiabatic path proposed by Saha *et al.* (6), the DFT calculation carried out by us predicted a non-adiabatic path (9). There is a small barrier for twisting in the *trans* isomer in the S₁ state to reach the perpendicular state (p*). The molecule decays from the p* state by a nonradiative path to the ground state *trans* and *cis* isomers. There is little or no bar-

rier for the *cis* isomers to reach the p* state. Therefore, the *cis* isomer is expected to fluoresce only in a rigid environment and to be nonfluorescent in fluid solution at room temperature. The fluorescence spectra of *t*-DMASBT were recorded in nonpolar dioxane, polar aprotic acetonitrile and polar protic viscous glycerol as a function irradiation time. In all the solvents the fluorescence intensities decrease, but no shift is observed in the fluorescence spectra (Fig. 4). The decreases in fluorescence intensities indicate the formation of *cis* isomer. If the adiabatic mechanism predicted by Saha *et al.* is correct, the radiative decay from excited *cis* isomer should result in blueshift upon irradiation. In fact, Saha *et al.* attributed the hypsochromic shift in the fluorescence spectrum of *t*-DMASBT in dioxane upon increasing the temperature to thermal isomerization (6). The absence of a spectral shift in the fluorescence spectrum of *t*-DMASBT upon isomerization (Fig. 4) substantiates the nonadiabatic path predicted by our TDDFT calculation for *t*-DMASBT. Our studies clearly establish that no shift is observed in the fluorescence spectra of *t*-DMASBT upon isomerization. Therefore, we attribute the small 4 nm hypsochromic shift observed in the fluorescence spectrum of *t*-DMASBT in dioxane by Saha *et al.* upon increasing the temperature to a thermochromic shift commonly observed in fluorescence spectra of dyes.

CONCLUSION

Contrary to the report of Saha *et al.*, the *trans*–*cis* photoisomerization of *t*-DMASBT competes with fluorescence not only in nonpolar solvents but also in polar and polar viscous solvents such as methanol and glycerol. The relatively high fluorescence quantum yield of *t*-DMASBT in glycerol is due to restriction by increased viscosity on the twisting of carbon–carbon double bond that leads to isomerization and not to restricted twisting from the TICT state as proposed earlier. The photoisomerization of *t*-DMASBT does not occur by an adiabatic path as previously proposed, but by a nonadiabatic path and the *cis* isomer is non-fluorescent in fluid solution at room temperature. DFT calculations predict that *cis*-B is stabilized by intramolecular hydrogen bonding under isolated condition.

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SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Figure S1. λ_{exc} dependence emission spectra of *t*-DMASBT (normalised) in chloroform (λ_{exc} value varies from 375 to 430 nm).

Figure S2. λ_{exc} dependence emission spectra of *t*-DMASBT (normalised) in dioxane (λ_{exc} value varies from 375 to 430 nm).

Figure S3. λ_{exc} dependence emission spectra of *t*-DMASBT (normalised) in acetonitrile (λ_{exc} value varies from 375 to 430 nm).

Figure S4. λ_{exc} dependence emission spectra of *t*-DMASBT (normalised) in methanol (λ_{exc} value varies from 375 to 430 nm).

Figure S5. λ_{exc} dependence emission spectra of *t*-DMASBT (normalised) in glycerol (λ_{exc} value varies from 375 to 430 nm).

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REFERENCES

- Mishra, A., R. K. Behera, P. K. Behera, B. K. Mishra and G. B. Behera (2000) Cyanines during the 1990's: A review. *Chem. Rev.* **100**, 1973–2012.
- Dekhtyar, M. and W. Rettig (2007) Charge-transfer transitions in twisted stilbenoids: Interchangeable features and generic distinctions of single- and double-bond twists. *J. Phys. Chem. A* **111**, 2035–2039.
- Sczepan, M., W. Rettig, A. I. Tolmachev and V. V. Kurdyukov (2001) The role of internal twisting in the photophysics of stilbazolum dyes. *Phys. Chem. Chem. Phys.* **3**, 3555–3561.
- Shaikh, M., J. Mohanty, P. K. Singh, A. C. Bhasikuttan, R. N. Rajule, V. S. Satam, S. R. Bendre, V. R. Kanetkar and H. Pal (2010) Contrasting solvent polarity effect on the photophysical properties of two newly synthesized aminostyryl dyes in the lower and in the higher solvent polarity regions. *J. Phys. Chem. A*, **114**, 4507–4519.
- Wang, S.-L. and T. -I. Ho (2000) Substituent effects on intramolecular charge-transfer behaviour of styrylheterocycles. *J. Photochem. Photobiol. A: Chem.* **135**, 119–126.
- Saha, S. K., P. Purkayastha and A. B. Das (2008) Excited state isomerization and effect of viscosity- and temperature-dependent torsional relaxation on TICT fluorescence of *trans*-2-[4-(dimethylamino)styryl] benzothiazole. *J. Photochem. Photobiol. A: Chem.* **199**, 179–187.
- Fayed, T. A. and S. S. Ali (2003) Protonation dependent photoinduced intramolecular charge transfer in 2-(*p*-dimethylaminostyryl) benzazoles. *Spectrosc. Lett.* **36**, 375–386.
- Saha, S. K., P. Purkayastha and A. B. Das (2008) Photophysical characterization and effect of pH on the twisted intramolecular charge transfer fluorescence of *trans*-2-[4-(dimethylamino)styryl]benzothiazole. *J. Photochem. Photobiol. A: Chem.* **195**, 368–377.
- Chipem, F. A. S., S. Chatterjee and G. Krishnamoorthy (2010) Theoretical study on photochemical behavior of *trans*-2-[4'-(dimethylamino)styryl]benzothiazole. *J. Photochem. Photobiol. A: Chem.* **214**, 121–127.
- Jaffer, S. S., M. Sowmiya, S. K. Saha and P. Purkayastha (2008) Defining the different phases of premicellar aggregation using the photophysical changes of a surface-probing compound. *J. Colloid Interface Sci.* **325**, 236–242.
- Sowmiya, M., A. K. Tiwari and S. K. Saha (2010) Fluorescence probe studies of micropolarity, premicellar and micellar aggregation of non-ionic brij surfactants. *J. Colloid Interface Sci.* **344**, 97–104.
- Jaffer, S. S., S. K. Saha, G. Eranna, A. K. Sharma and P. Purkayastha (2008) Intramolecular charge transfer probe induced formation of α -cyclodextrin nanotubular suprastructures: A concentration dependent process. *J. Phys. Chem. C* **112**, 11199–11204.
- Sowmiya, M., P. Purkayastha, S. K. Saha and S. S. Jaffer (2009) Characterization of guest molecule concentration dependent nanotubes of β -cyclodextrin and their secondary assembly: Study with *trans*-2-[4-(dimethylamino)styryl]benzothiazole, a TICT-fluorescence probe. *J. Photochem. Photobiol. A: Chem.* **205**, 186–196.
- Jaffer, S. S., S. K. Saha and P. Purkayastha (2009) Fragmentation of molecule-induced γ -cyclodextrin nanotubular suprastructures due to drug dosage. *J. Colloid Interface Sci.* **337**, 294–299.
- Das, T., A. Kumar, P. Ghosh, A. Maity, S. S. Jaffer and P. Purkayastha (2010) Interaction of twisted intramolecular charge-transfer probe loaded silver nanoparticles with the hydrophobic nanocavities of cyclodextrins. *J. Phys. Chem. C* **114**, 19635–19640.
- Maity, A., S. S. Jaffer, T. Das, P. Ghosh and P. Purkayastha (2011) Orientation of a TICT probe trapped in the peripheral confined water created by ionic surfactant envelope around silver nanoparticles. *Langmuir* **27**, 4068–4075.
- Frisch, M. J., G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople (2004) *Gaussian 03, Revision E.01*. Gaussian Inc., Wallingford, CT.
- Hohenberg, P. and W. Kohn (1964) Inhomogeneous electron gas. *Phys. Rev. B* **136**, 864–871.
- Kohn, W. and L. J. Sham (1965) Self-consistent equations including exchange and correlation effects. *Phys. Rev. A* **140**, 1133–1138.
- Becke, A. D. (1993) Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652.
- Lee, C., W. Yang and R. G. Parr (1988) Development of the Colle–Savetti correlation-energy formula into a functional of the electron-density. *Phys. Rev. B* **37**, 785–789.
- Casida, M. E. (1995) Time-dependent density functional response theory for molecules. In *Recent Advances in Density Functional Methods Part I* (Edited by D. P. Chong), pp. 155–192, World Scientific, Singapore.
- Gross, E. K. U., J. F. Dobson and M. Petersilka (1996) Density functional theory of time-dependent phenomena. *Top. Curr. Chem.* **118**, 81–172.
- Malkin, S. and E. Fischer (1964) Temperature dependence of photoisomerization. III. Direct and sensitized photoisomerization of stilbenes. *J. Phys. Chem.* **68**, 1153–1163.
- Waldeck, D. H. (1991) Photoisomerization dynamics of stilbene. *Chem. Rev.* **91**, 415–436.
- Saltiel, J. and J. T. D. Agostino (1972) Separation of viscosity and temperature effects on the singlet pathway to stilbene photoisomerization. *J. Am. Chem. Soc.* **94**, 6445–6456.
- Saltiel, J. and Y.-P. Sun (1989) The intrinsic potential energy barrier for twisting in the *trans*-stilbene S1 state in hydrocarbon solvents. *J. Phys. Chem.* **93**, 6246–6250.
- Saltiel, J., A. S. Waller, D. F. Sears Jr., E. A. Hoburg, D. M. Zeglin-ski and D. H. Waldeck (1994) Fluorescence quantum yields and lifetimes of substituted stilbenes in *n*-alkanes. A reexamination of the relationship between solute size and medium effect on torsional relaxation. *J. Phys. Chem.* **98**, 10689–10698.
- Saltiel, J., W. , A. , S. , Y.-P. and D. F. Sears Jr. (1990) *Cis*-stilbene fluorescence in solution. Adiabatic c^* to t^* conversion. *J. Am. Chem. Soc.* **112**, 4580–4581.
- Saltiel, J., A. S. Waller and D. F. Sears Jr. (1992) Dynamics of *cis*-stilbene photoisomerization: The adiabatic pathway to excited *trans*-stilbene. *J. Photochem. Photobiol. A: Chem.* **65**, 29–40.
- Saltiel, J., A. S. Waller and D. F. Sears Jr. (1993) The temperature and medium dependencies of *cis*-stilbene fluorescence. The energetics for twisting in the lowest excited singlet state. *J. Am. Chem. Soc.*, **115**, 2453–2465.
- Sharafy, S. and K. A. Muszka (1971) Viscosity dependence of fluorescence quantum yields. *J. Am. Chem. Soc.* **93**, 4119–4125.
- Dugave, C. and L. Demange (2003) *Cis-trans* isomerization of organic molecules and biomolecules: Implications and applications. *Chem. Rev.* **103**, 2475–2532.
- Jacobs, H. J. C. and E. Havinga (1979) Photochemistry of vitamin D and its isomers and of simple trienes. *Adv. Photochem.* **11**, 305–373.
- Saltiel, J., D. F. Sears Jr., J.-O. Choi, Y.-P. Sun and D. W. Eaker (1994) The fluorescence, fluorescence-excitation and UV absorption spectra of *trans*-1-(2-naphthyl)-2-phenylethene conformers. *J. Phys. Chem.* **98**, 35–46.