



Theoretical study on thermal *cis*-to-*trans* isomerization of BF₂-coordinated azo compounds of the para-substitution with electron donating groups



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ABSTRACT

Thermal *cis*→*trans* isomerization for a series of BF₂-coordinated azo compounds of the para-substitution with electron donating groups have been systematically investigated. The density-functional theory calculations exhibited good performance to provide better understanding of the effects of para-substitution with electron donating groups. It is found that the different electron donation groups can significantly affect the absorption spectra, the energy levels of molecular orbitals, the transition properties for the *trans* isomers, the rate constants and the half-lives for the thermal *cis*→*trans* isomerization. Our calculated half-lives for the thermal *cis*→*trans* isomerization are in qualitative agreement with the experimental values. Specifically, we have evaluated the thermal rate constants at 294 K. The relationship between the thermal isomerization and the para-substituted electron-donating group reveals that the inversion mechanism is preferred for the substituent species while the rotation mechanism is more favorable for non-para-substituent molecule.

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1. Introduction

Since 1937 [1,2], a large number of azobenzene derivatives have been used extensively in materials [3–6] and biochemical [7–9] sciences, due to their reversible photo and thermal isomerization properties between two isomeric forms. Lots of the π -system of azo compounds can be easily synthesized and modified, resulting in the large variations in the shape of their configuration, the profiles of their absorption spectra, the relative energetic order of their π → π^* and n → π^* transitions, and the isomerization reactions between the *trans*- and *cis*-isomers as molecular switches (MSS) in the ultraviolet (UV) light region or others [10].

For most of the up-to-date applications, however, the performance of visible and Near-Infrared (NIR) lights in the system of the MSS are far better than UV light [11]. There are two drawbacks of UV light that generally limits the development of the MSS in vivo applications: (i) the penetration of UV light in the surface of cells, tissues, and organic materials is difficult, owing to it is strongly

scattered [12,13]. (ii) The short wavelength of UV light can severely damage the corresponding surfaces [14,15]. Therefore, the development of the MSS that can avoid the irradiation with UV light is highly desirable. Specifically, various strategies [10,12,16–18], that take advantage of visible or NIR light, such as (i) the large separation of n → π^* transitions, (ii) the red-shift of the π → π^* band, (iii) the activation wavelength of the added metal-to-ligand charge transfer (MLCT) is being red-shifted, and (iv) the lower energy of n → π^* transitions compared to π → π^* transitions, have been used to accomplish this goal. With these strategies utilized, a series of Azo compounds were synthesized and/or modified, including: Herges [16], Woolley [12], and Bléger [17] that are all based on the related strategy (i) with azobenzene (AB) functionalized in the ortho positions that covalently bridged by an ethylene linker, four methoxy groups and four fluorine groups, respectively. Arahamian in the BF₂-coordinated azo compound using the strategy (iv) in contrast to conventional AB is reported [10]. An interesting but debating approach is that the π_{nb} (*nonbonding*)→ π^* transition is shifted to the visible range by coordinating the azo group's n-electrons with Lewis acids [10].

In addition, the *cis*→*trans* isomerization for azo compounds is achievable with either a thermal process or a photochemical

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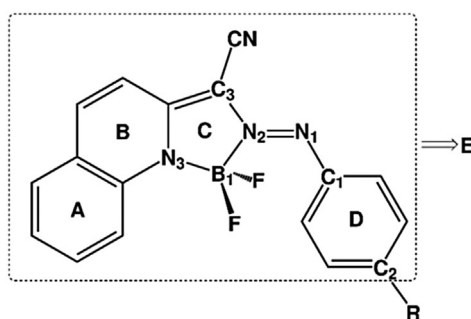
process. Namely, the isomerization reaction from *cis* → *trans* can be achieved thermally in gas or condensed phase [19]. Moreover, this behavior results in a highly efficient *cis* → *trans* isomerization process that can be converted spontaneously in the dark, due to the higher stability of the *trans* isomer than corresponding *cis* isomer [20]. In order to explain the thermal *cis* → *trans* isomerization thoroughly, several mechanisms have been proposed for AB and its derivatives, including: inversion, rotation, concerted inversion, rotation-assisted inversion, and inversion-assisted rotation [15,19,21–24]. The change of the conventional azo group (-N=N-) for the thermal process involves the two N–N–C angles and the C–N–N–C dihedral angle. Interestingly, the coordination of BF₂ with an azo group's nitrogen only leads to the alteration of N–N–C angle and C–N–N–C dihedral angle (see Fig. 1). Therefore, the *cis* → *trans* thermal isomerization can be controlled easily. Aprahamian and co-workers have described the BF₂-coordinated azo compounds (BF₂S) with electron donating groups (EDGs) in the para position of the phenyl ring that can be controlled with the near-infrared (NIR) light only [25]. The corresponding mechanisms of the thermal isomerization of BF₂-coordinated azo compound are investigated in this work theoretically and systematically as reasonable supplement.

The goal of present paper is to provide a systematic approach to better understand the effects of EDGs as the substituent at the para position of the phenyl ring, as well as an effort for using strong

electron donating for investigating the effect of absorption spectra at room temperature (298.15 k) and thermal *cis* → *trans* isomerization convert back in the dark at 294 k in DFT study, in which the calculation values show highly agreement with the corresponding experimental results [10,25].

2. Computational details

Quantum chemical calculations were done using the Gaussian 09 package of program [26]. All stationary-point geometries (equilibrium configurations and transition-state structures) were computed using ab initio density-functional theory (DFT) [27,28] with the B3LYP functional [29]. As a further test, several other functionals (PBE0 [30], M06-2X [31], CAM-B3LYP [32], and M06 [31]) were employed to compare and avoid the shortcomings of DFT methods in the gas-phase environment (see Table S1). Moreover, the 6-31 + G(d) basis set was adopted for all atoms based on the test of basis sets and computational costs consideration (Table S2). Solvent interactions were simulated using a polarizable continuum model (PCM) [33], with parameters taken from the CH₂Cl₂. The natural bonding orbitals (NBO) analysis [34] was performed using NBO 3.1 program as implement in the Gaussian 09 package. Furthermore, all geometrical structures of the transition states (TS), *cis* and *trans* forms were fully re-optimized in the CH₂Cl₂. In particular, all the computations were carried out using



	R-H	R-pyrrolidinyl	R-methylpiperazinyl	
1		4	7	
	R-methoxyl	R-piperidinyl		
2		5		
	R-dimethylaminyl	R-morpholinyl		
3		6		
compound abbreviation	E-H BF ₂ -H	E-methoxyl BF ₂ -OMe	E-dimethylaminyl BF ₂ -NMe ₂	E-pyrrolidinyl BF ₂ -PYY
compound abbreviation	E-piperidinyl BF ₂ -PIY	E-morpholinyl BF ₂ -MOY	E-methylpiperazinyl BF ₂ -MEP	

Fig. 1. Structures of the investigated molecules and the corresponding substituents.

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