



# Isomerization and electronic relaxation of azobenzene after being excited to higher electronic states

Luoxin Wang<sup>a,\*</sup>, Weilin Xu<sup>a</sup>, Changhai Yi<sup>a</sup>, Xiaogong Wang<sup>b</sup>

<sup>a</sup> Key Laboratory of Green Processing and Functional Textiles of New Textile Materials (Wuhan University of Science and Engineering), Ministry of Education, Wuhan 430073, PR China

<sup>b</sup> Department of Chemical Engineering, Laboratory for Advanced Materials, Tsinghua University, Beijing 100084, PR China

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## ABSTRACT

In this work, some critical structures (e.g. stable structure, transition state, local minimum and conical intersection) of azobenzene photoisomerization were optimized by means of *ab initio* CASSCF calculation. The potential energy surfaces for the CNNC dihedral torsion and CNN bond angle concerted-inversion pathway were mapped to explore the relaxation process of azobenzene (AB) photoisomerization. The results indicate that the rotational mechanism favors the photoisomerization of the  $S_1(n,\pi^*)$  and  $S_2(\pi,\pi^*)$  *trans*-AB. The concerted-inversion mechanism may operate in the decay process of  $S_2(\pi,\pi^*)$  or higher state *trans*-AB. By borrowing the  $(n,\pi^*; \pi,\pi^*)$  and  $(n^2,\pi^{*2})$  electronic states, *trans*-AB upon excitation to the higher states can quickly relax to the  $S_1(n,\pi^*)$  or ground state via the rotation or concerted-inversion pathway. The forming ground-state species with higher vibrational energy from the higher excited states will become the stable *trans*-isomer through the concerted-inversion pathway. These relaxation processes have been confirmed by the conical intersections calculated by the high-level CASSCF method.

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## 1. Introduction

Organic or inorganic materials based on the azobenzene (AB) unit have attracted significant attention because of their photoresponsive properties that arise from the reversible *cis*–*trans* photoisomerization of AB [1–10]. Accordingly, the photochemistry and photophysics of AB is again becoming a research focus in recent years [11–15]. An important subject is the photoisomerization mechanism of AB, which has been debated for a long time. It is well known that azobenzene has two important absorption bands: a weak band in the visible light region corresponding to the  $n \rightarrow \pi^*$  electronic transition and an intense band in the UV spectral region corresponding to  $\pi \rightarrow \pi^*$  electronic transition. An argument about photoisomerization mechanism of AB initially originated from the following experimental observation: the quantum yield ( $\Phi$ ) of *trans*  $\rightarrow$  *cis* isomerization is 0.20–0.36 upon excitation to the  $S_1(n,\pi^*)$  state and it decreases to 0.09–0.20 when excitation to the  $S_2(\pi,\pi^*)$  state [16]. The dependence of  $\Phi$  on the excitation wavelength obviously violates Kasha's rule. Therefore, two photoisomerization pathways (rotation around the NN double bond on the  $S_2(\pi,\pi^*)$  state and inversion of CNN angle on the

$S_1(n,\pi^*)$  state) were firstly proposed by Rau and Lüddecke to explain this violation [17].

Rau's photoisomerization model has been successfully applied to explain the time-resolved spectrum measurements on the excited-state decay dynamics of azobenzene and its derivatives [18–23]. However, some new experimental and high-level theoretical results challenge this original model. The picosecond time-resolved Raman and femtosecond time-resolved fluorescence spectroscopy have been applied to investigate the photoisomerization of *trans*-AB [24,25]. The results indicate that the NN bond retains a double bond nature and the molecule keeps a planar structure in the  $S_1(n,\pi^*)$  state. The isomerization of AB only concerns the inversion mechanism occurring on the  $S_1(n,\pi^*)$  state, and the rotational isomerization pathway starting directly from the  $S_2(\pi,\pi^*)$  state does not exist. Recently, *ab initio* and density-functional calculations have been used to study the isomerization mechanism of azobenzene. The results show that the  $S_1(n,\pi^*)$  state decay mainly involves the rotation mechanism [26–28]. Meanwhile, another concerted-inversion relaxation channel for the  $S_1(n,\pi^*)$  excited *trans*-AB was found through *ab initio* calculations [29]. Presumably this concerted-inversion channel is inclined to produce more *trans*-isomers after *trans*-AB is excited to the  $S_2(\pi,\pi^*)$  state or higher vibration energy level of the  $S_1(n,\pi^*)$  state. The concerted-inversion channel has also been supported by the femtosecond fluorescence anisotropy study [30].

\* Corresponding author. Tel.: +86 27 87426559; fax: +86 27 87426559.  
E-mail address: [wanglx@wuse.edu.cn](mailto:wanglx@wuse.edu.cn) (L. Wang).

In contrast to the extensive discussion on the  $S_1(n,\pi^*)$  state, the thorough understanding of the  $S_2(\pi,\pi^*)$  state still lacks. In several previous papers [23,25,31], it has been reported that the AB molecule can quickly decay from  $S_2(\pi,\pi^*)$  state to the  $S_1(n,\pi^*)$  state. The  $S_2(\pi,\pi^*)$  state with a lifetime of 110–170 fs was determined by the time-resolved spectroscopy measurements. A semiclassical dynamics approach has been recently applied to simulate the potential energy surfaces (PES) and the photoisomerization dynamics of AB [32]. The result shows that the torsion around the NN double bond is the preferred mechanism upon excitation on the  $S_1(n,\pi^*)$  or  $S_2(\pi,\pi^*)$  state. Moreover, two conical intersections (CI) between  $S_1(n,\pi^*)$  and  $S_2(\pi,\pi^*)$  state were found with the transoid and cisoid geometries, respectively. It is easy for the  $S_2(\pi,\pi^*)$  FC species to access these conical intersections because of small geometrical distortions and energy demanded. By means of *ab initio* CASSCF calculation, it has been shown that by borrowing another singlet state that gets significant contributions of doubly excited configuration ( $n^2,\pi^{*2}$ ),  $S_2(\pi,\pi^*)$  state can rapidly relax to the  $S_1(n,\pi^*)$  state [27,33]. That is to say, some other excited electronic states could play an important role in the decay process of AB after excitation to  $S_2(\pi,\pi^*)$  state.

At the current stage, it seems that a general conclusion has been drawn for the isomerization mechanism and decay dynamics of AB on the  $S_1(n,\pi^*)$  state, but there is still an insufficiency of understanding the details of AB on the  $S_2(\pi,\pi^*)$  state. In fact, the decay dynamics and isomerization mechanism of AB on the  $S_2(\pi,\pi^*)$  state are of more interest for the reason that the photoresponsive properties of materials containing AB are commonly modulated by the UV light ( $\sim 365$  nm) that corresponds to the maximum absorption wavelength ( $S_0 \rightarrow S_2(\pi,\pi^*)$  transition) of AB [34–36]. Therefore, it is necessary to further map the thorough PES of higher excited states along CNNC rotation and CNN inversion coordinates and focus on the details in the cross-region between different excited states.

In the present study, through a high-level *ab initio* calculation, we scanned the PES of the first five singlet states along the CNN inversion coordinate and optimized some important points on the CNNC rotational pathway. Some CIs between two different electronic states were also optimized. The important features of the PES were described in detail in order to comprehensively understand the relaxation process of  $S_2(\pi,\pi^*)$  state. The calculation strategy, the main results and discussion will be given in the following sections

## 2. Calculation strategy

In this work, all the computations were carried out by means of CASSCF method encapsulated in the Gaussian 03 software [37]. CASSCF calculation has been widely used to deal with the excited states relevant to photochemical and photophysical processes [38]. It can give accurate descriptions of the PESs in both the ground and excited states [39–44]. The optimization of the stable structures and transition states were performed at the state-specific CASSCF level. The state-average CASSCF calculation with equal weights was used to determine the geometries of conical intersections (CIs). The PESs of the first five singlet states along the CNN inversion coordinates were obtained at the state-average CASSCF level, in which the  $S_0$  PES was scanned firstly and then energies of each electronic state were recomputed with single-point calculations on the basis of the geometries of the  $S_0$  PES. The 6-31G\* basis set was employed in all the CASSCF calculations.

Theoretically, the active space should contain all of the valence electrons and orbitals for the CASSCF calculation. Due to the limitation of the computational power, it is difficult to do so for azobenzene. Therefore, choosing the active space becomes a crucial step in the CASSCF calculations. According to the previous

calculations on the photoisomerization reaction of azobenzene, the active space including six electrons distributed among six orbitals, referred as to CAS(6,6), can reasonably map the PES of photoisomerization on the ground state and three excited states [45]. In this study, we chose an active space of ten electrons in eight orbitals, namely CAS(10,8), in order to describe more excited states and not heavily increase the calculation workload at the same time. These orbitals included the  $\pi$  and  $\pi^*$  orbitals of  $-N=N-$  group, two non-bonding orbitals occupied by two lone-pair electrons ( $n_+$ ,  $n_-$ ) of  $-N=N-$  group, and two  $\pi$  and  $\pi^*$  orbitals of the aromatic ring.

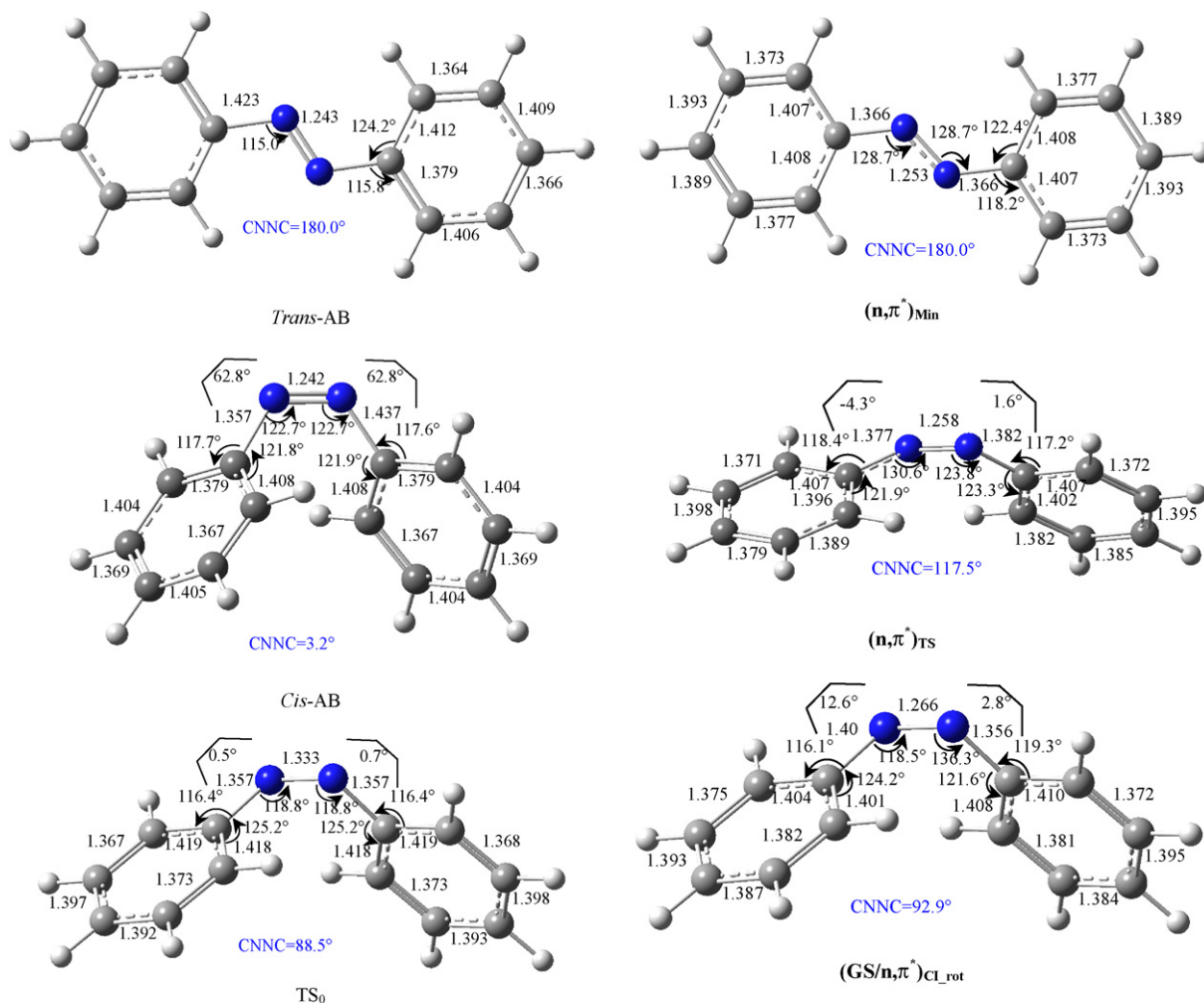
## 3. Results and discussion

### 3.1. Rotational pathway

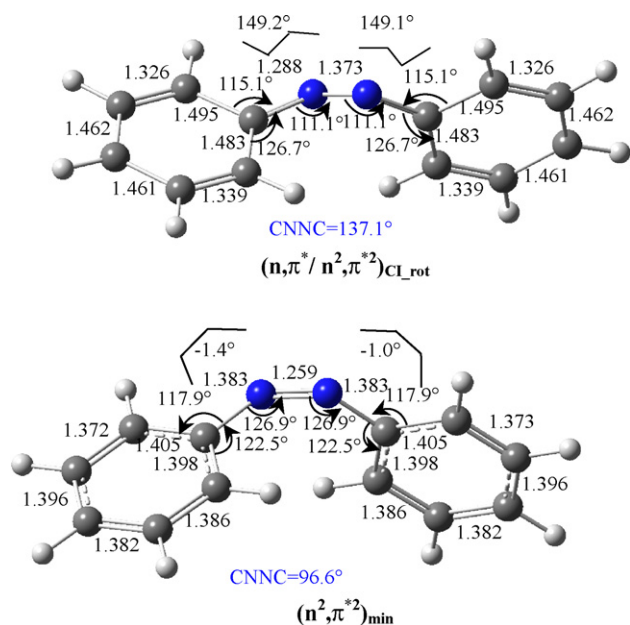
In the previous studies [26,27,29], it has been found that the rotational mechanism is most favorable in energy for the isomerization of AB on the  $S_1(n,\pi^*)$  state. In this study, we also optimized the important structures involved in this rotational isomerization channel at the CAS(10,8)/6-31G\* level of theory. The detailed geometries of all the structures, shown in Fig. 1, are in a good agreement with the results reported by Cembran et al. [26]. For example, the *trans*-AB with  $C_{2h}$  symmetry has the energy of 16.2 kcal/mol lower than that of the *cis*-AB with  $C_2$  symmetry. A local  $S_1$  minimum,  $(n,\pi^*)_{\min}$ , with a planar configuration and a transition state,  $(n,\pi^*)_{TS}$ , with the CNNC dihedral of  $117.5^\circ$  were also found on the  $S_1(n,\pi^*)$  state. The energy of  $(n,\pi^*)_{\min}$  is very similar to that of the  $(n,\pi^*)_{TS}$ . A conical intersection between the ground state and the  $S_1(n,\pi^*)$  state,  $(GS/n,\pi^*)_{CI_{rot}}$ , was found to locate on the middle of the PES along the CNNC rotational coordinate. This CI shows a twisted geometry with the CNNC dihedral of about  $93^\circ$ . All the above characteristics further indicate that a rotational pathway indeed plays an important role in the isomerization process of AB on the  $S_1(n,\pi^*)$  state.

We attempted to optimize the key structures on the  $S_2(\pi,\pi^*)$  state, such as local minimum, transition state and the conical intersection, in order to understand the energy decay pathway of AB once it is excited on the  $S_2(\pi,\pi^*)$  state. However, all the attempts to optimize these structures relevant to the  $S_2(\pi,\pi^*)$  state failed because of the convergence problem. It has been found that the energy of  $S_2(\pi,\pi^*)$  *trans*-FC point is very close to that of the  $(\pi_p,\pi^*)$  FC point [31]. The  $(\pi_p,\pi^*)$  electronic state corresponds to the transition of  $\pi$  electron of phenyl ring to the  $\pi^*$  orbital of  $-N=N-$  group. Our calculation also showed that slight changes in the geometries of *trans*-AB could easily induce the overlap of the  $S_2(\pi,\pi^*)$ ,  $(n^2,\pi^{*2})$ ,  $(\pi_p,\pi^*)$  and  $(n,\pi^*; \pi,\pi^*)$  electronic states in the vicinity of the FC region, which can be seen clearly in the following concerted-inversion PES. Therefore, the electronic states can readily flip and convergence fails during the process of optimization, which may be one of the reasons why the details of the  $S_2(\pi,\pi^*)$  state are insufficient at the present stage. Because of the hop of different electronic states in the vicinity of  $S_2(\pi,\pi^*)$  *trans*-FC region, *trans*-AB on the  $S_2(\pi,\pi^*)$  state can rapidly decay to the other electronic state, e.g.  $(n,\pi^*; \pi,\pi^*)$  and  $(n^2,\pi^{*2})$  states, through the small bending of two CNN angles. Based on the above analysis, we examined the  $(n^2,\pi^{*2})$  electronic state and found a local minimum,  $(n^2,\pi^{*2})_{\min}$ , and a conical intersection,  $(n,\pi^*/n^2,\pi^{*2})_{CI_{rot}}$ . Fig. 2 gives the geometrical parameters of the two structures. Apparently, these two structures belong to the key point of rotational isomerization pathway because of their twisted configuration.

The energies of all the structures shown in Figs. 1 and 2 are listed in Table 1. It should be noted that the CASSCF energies are 18–35 kcal/mol greater than experiment excitation energies because dynamic correlation energy is not included, but the energetic ordering agrees with the experiment and DFT calculation



**Fig. 1.** Some important structures of azobenzene on the rotational PES of the ground state (GS) and  $S_1(n, \pi^*)$  state. The bond length is in angstrom and the bond angle is in degree.



**Fig. 2.** Some important structures of azobenzene concerning the  $(n^2, \pi^{*2})$  electronic state. The bond length is in angstrom and the bond angle is in degree.

[31]. By comparing these energies of FC and conical intersection and combining with the literature result [26,27], a preliminary sketch about the rotational isomerization PES of AB on the  $S_1(n, \pi^*)$  and  $S_2(\pi, \pi^*)$  states is constructed and shown in Fig. 3. It is clearly shown from this scheme that when being excited to the  $S_1(n, \pi^*)$ ,

**Table 1**

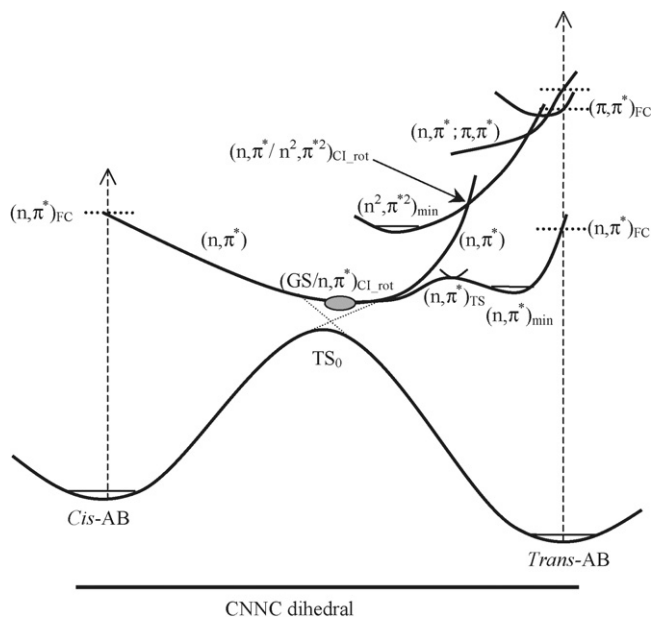
The energies of all the structures on the rotational PES of azobenzene.

Structure	Energy (a.u.)
<i>Trans-AB</i>	−569.17001
<i>Cis-AB</i>	−569.14421
<i>Cis-S<sub>1</sub>(n,π*)<sub>FC</sub></i>	−569.01366 <sup>a</sup>
<i>Trans-S<sub>1</sub>(n,π*)<sub>FC</sub></i>	−569.03940 <sup>b</sup>
<i>Trans-S<sub>2</sub>(π,π*)<sub>FC</sub></i>	−568.93175 <sup>b</sup>
<i>Trans-(n,π*;π,π*)<sub>FC</sub></i>	−568.92806 <sup>b</sup>
<i>Trans-(π<sub>p</sub>,π*)<sub>FC</sub></i>	−568.91860 <sup>b</sup>
<i>TS<sub>0</sub></i>	−569.09042
<i>(n,π*)<sub>min</sub></i>	−569.06886
<i>(n,π*)<sub>TS</sub></i>	−569.06554
<i>(GS/n,π*)<sub>CI_rot</sub></i>	−569.07344 (GS)
	−569.07335 ( <i>n,π*</i> )
<i>(n,π*/n²,π²²)<sub>CI_rot</sub></i>	−568.96572 ( <i>n²,π²²</i> ) <sup>c</sup>
	−568.96561 ( <i>n,π*</i> ) <sup>c</sup>
<i>(n²,π²²)<sub>min</sub></i>	−569.04477

<sup>a</sup> State-average factors  $S_0/S_1$ : 0.5/0.5.

<sup>b</sup> State-average factors  $S_0/S_1/S_2/S_3/S_4$ : 0.2/0.2/0.2/0.2/0.2.

<sup>c</sup> State-average factors  $S_0/S_1/S_2$ : 0.0/0.5/0.5.



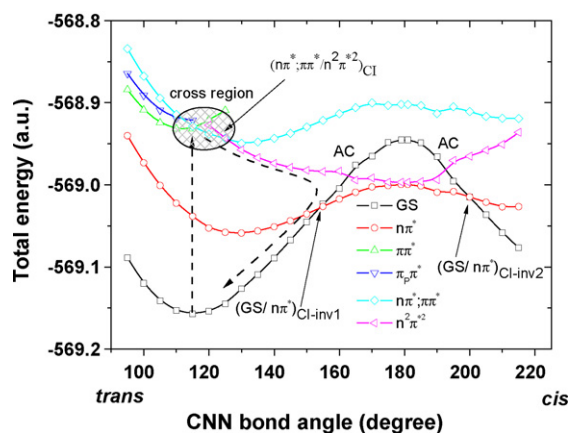
**Fig. 3.** Schematically rotational PES of azobenzene after excitation to the  $S_1(n,\pi^*)$  and  $S_2(\pi,\pi^*)$  states.

AB will decay to the  $(GS/n,\pi^*)_{CI\_rot}$  by the rotation of CNNC dihedral and the trans–cis isomerization is likely to occur finally. This process is favorable in energy. In the case of *trans*-AB being excited on the  $S_2(\pi,\pi^*)$  state, borrowing the  $(n,\pi^*; \pi,\pi^*)$  and  $(n^2,\pi^{*2})$  electronic states, *trans*-AB may rapidly relax to the  $S_1(n,\pi^*)$  state. During this relaxation process, the CNNC dihedral will twist from  $180^\circ$  to about  $137^\circ$ . Along with the further twisting of CNNC dihedral, the species on the  $S_1(n,\pi^*)$  state can decay to the ground state through the  $(GS/n,\pi^*)_{CI\_rot}$  and some *cis*-AB would come into being ultimately. That is to say, when photoexcitation occurs in the  $S_1(n,\pi^*)$  or  $S_2(\pi,\pi^*)$  state, there exists a rotational isomerization pathway for *trans*-AB. However, whether this rotational pathway also operates for the *cis*-AB after excitation to the  $S_2(\pi,\pi^*)$  state still needs to be further studied.

### 3.2. Concerted-inversion pathway

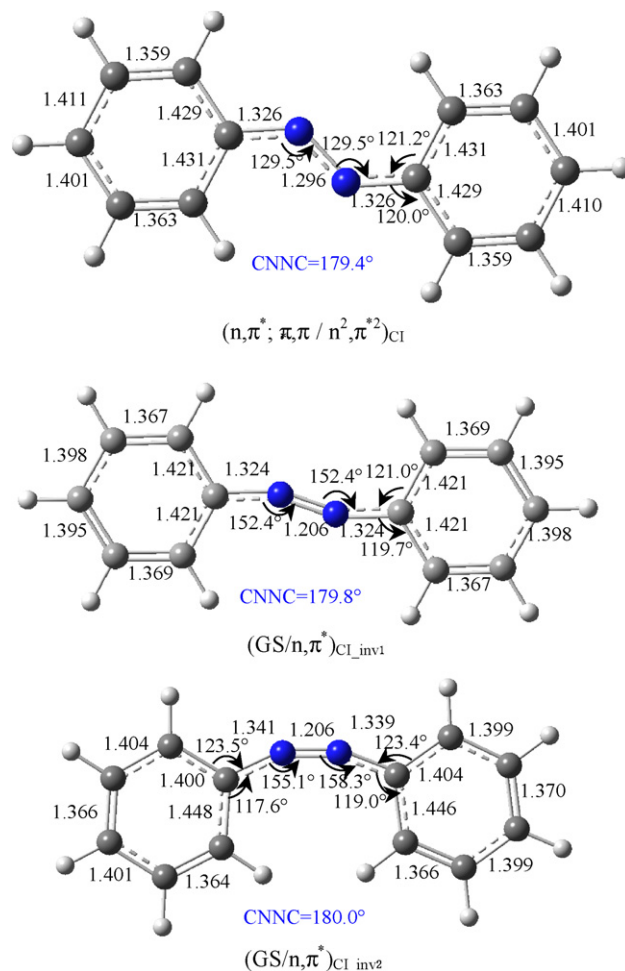
On the basis of the theoretical calculation, Diao has found that there is another decay pathway (concerted-inversion pathway) on the  $S_1(n,\pi^*)$  state [29]. The conical intersection,  $(GS/n,\pi^*)_{CI\_inv}$ , on this concerted-inversion pathway has higher energy than the  $S_1(n,\pi^*)$  *trans*-FC point. Therefore, the “cold”  $S_1(n,\pi^*)$  *trans*-species cannot decay the electronic excitation energy via this concerted-inversion channel. Only when being excited to the  $S_2(\pi,\pi^*)$  or higher electronic state, the concerted-inversion channel may be open and the  $(GS/n,\pi^*)_{CI\_inv}$  will become energetically accessible to give more products with *trans*-configuration. Nevertheless, it is still unclear that how the *trans*-AB on the higher excited state relaxes to the  $(GS/n,\pi^*)_{CI\_inv}$ . To address this question, we scanned the PESs of five electronic state along the synchronous bending of two CNN angles and found a new relaxation route of *trans*-AB from the higher excited state down to the  $(GS/n,\pi^*)_{CI\_inv}$ . This relaxation process involves the cross of several electronic states and a cross-region exists in the vicinity of *trans*-FC point as seen in Fig. 4.

Along the coordinates relevant to the synchronous bending of two CNN angles, the concerted-inversion decay pathway involves a quick switch from the  $S_2(\pi,\pi^*)$  and  $(\pi_p,\pi^*)$  states to the  $(n,\pi^*; \pi,\pi^*)$  double electronic state, followed by the subsequent decay to the  $(n^2,\pi^{*2})$  state through a conical intersection,  $(n,\pi^*; \pi,\pi^*/n^2,\pi^{*2})_{CI}$ . As mentioned before, however, due to the degenerate



**Fig. 4.** Concerted-inversion PESs of azobenzene along the two CNN bond angles.

energy of these several excited states in the FC region and the convergence problem during the process of optimization, we failed to optimize the CIs among the  $S_2(\pi,\pi^*)$ ,  $(\pi_p,\pi^*)$  and  $(n,\pi^*; \pi,\pi^*)$  states. Only a CI between the  $(n,\pi^*; \pi,\pi^*)$  and  $(n^2,\pi^{*2})$  states was successfully obtained and it shows a planar structure (seen in Fig. 5). As for the  $S_2(\pi,\pi^*)$  state, to rapidly decay to the other states means that its lifetime is very short, which is in a good agreement with the time-resolved spectroscopy measurements. Experimentally, the observed lifetime of  $S_2(\pi,\pi^*)$  state was about 110–170 fs [23,25,31].



**Fig. 5.** Some important structures of azobenzene on the concerted-inversion PESs.



Decay from *trans*-FC point to the  $(n, \pi^*; \pi, \pi^*/n^2, \pi^{*2})_{\text{CI}}$  not only needs  $\sim 15^\circ$  bending of two CNN angles and the stretching of NN bond but also induces the deformation of phenyl rings. This can be seen from the differences between the geometries of *trans*-AB and the  $(n, \pi^*; \pi, \pi^*/n^2, \pi^{*2})_{\text{CI}}$ . Further along the bending coordinates of two CNN angles, we found that the crossing between the ground state and the  $(n^2, \pi^{*2})$  state took place at  $\sim 160^\circ$  of CNN angle. The calculation result suggests that this is a weakly avoided crossing point because the energetic difference of the two states was calculated to be about 6 kcal/mol. Evidently, through this CI point, the vibrationally hot ground-state molecule can come directly back to the stable structure by means of the energy exchange with the environment. On the other hand, due to significantly higher energy, the species going through the  $(n, \pi^*; \pi, \pi^*/n^2, \pi^{*2})_{\text{CI}}$  can also relax to the  $(\text{GS}/n, \pi^*)_{\text{CI\_inv1}}$ . Fig. 4 clearly shows the process of *trans*-AB from  $S_2(\pi, \pi^*)$  FC point to the  $(\text{GS}/n, \pi^*)_{\text{CI\_inv1}}$ . As discussed before, funneling through the  $(\text{GS}/n, \pi^*)_{\text{CI\_inv1}}$  will produce more *trans*-AB eventually.

Fig. 4 also provides some information about the relaxation pathway of *cis*-AB excitation on the higher electronic state. *cis*-AB can also decay to the  $S_1(n, \pi^*)$  or ground state by borrowing the  $(n^2, \pi^{*2})$  state. A conical intersection,  $(\text{GS}/n, \pi^*)_{\text{CI\_inv2}}$ , with the *cis*-configuration of CNNC dihedral was successfully optimized. It is found that this CI also owns a planar structure, which can be seen from Fig. 5. Funneling through this conical intersection, the species with *cis*-configuration of CNNC dihedral might take place along with the rotation of phenyl rings around the CN bond because of higher potential energy. However, a comprehensive study is required to understand this dynamic process as well as relaxation paths of *cis*-AB. The relevant studies are underway in our laboratory.

#### 4. Conclusions

In this study, we have optimized some important points, such as stable structure, transition state, local minimum and conical intersection, on the relaxation pathway of azobenzene photoisomerization. The potential energy surfaces along the rotational coordinate of CNNC dihedral and the concerted-inversion coordinates of CNN angles have been constructed. Our computation results suggest that the rotational decay pathway plays a key role in the photoisomerization of *trans*-AB once being excited on the  $S_1(n, \pi^*)$  or  $S_2(\pi, \pi^*)$  state. In addition, another decay pathway involves the concerted-inversion of two CNN angles, in which the  $S_2(\pi, \pi^*)$  or  $(\pi_p, \pi^*)$  states of *trans*-AB can quickly switch to the  $(n, \pi^*; \pi, \pi^*)$  state, and then to the  $(n^2, \pi^{*2})$  double electronic state. Ultimately, the  $(n^2, \pi^{*2})$  can directly cross with the ground state. In this case, the forming ground-state species with higher energy will become the stable *trans*-isomer either through  $(\text{GS}/n, \pi^*)_{\text{CI\_inv1}}$  or interconversion. Our results make a contribution to the understanding of the isomerization mechanism and electronic relaxation of AB after excitation to the higher states.

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