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Comparative Studies of the *trans*–*cis* Photoisomerizations of Azobenzene and a Bridged Azobenzene

Chen-Wei Jiang,^{†,‡} Rui-Hua Xie,^{†,§} Fu-Li Li,[†] and Roland E. Allen^{*,‡}

Ministry of Education (MOE) Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, and Department of Applied Physics, Xi'an Jiaotong University, Xi'an 710049, China, Department of Physics, Texas A&M University, College Station, Texas 77843, United States, and Department of Physics, Hubei University, Wuhan 430062, China

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Using density-functional-based molecular dynamics simulations, we have performed comparative studies of the *trans*–*cis* isomerizations of azobenzene and bridged azobenzene (B-Ab) 5,6-dihydrodibenzo[*c,g*]-[1,2]diazocine induced by $n\pi^*$ electronic excitation. The quantum yields found in our calculations, 45% for the bridged azobenzene versus 25% for azobenzene, are consistent with the experiment. Both isomerization processes involve two steps: (1) Starting from the *trans* structure, each molecule moves on its S_1 excited-state potential energy surface, via rotation around the NN bond, to an avoided crossing near the S_1/S_0 conical intersection, where de-excitation occurs. (2) Subsequently, in the electronic ground state, there is further rotation around the NN bond, accompanied by twisting of the phenyl rings around their CN bonds, until the *cis* geometry is achieved. Because of its lower symmetry and smaller initial CNNC dihedral angle, the bridged azobenzene has a much shorter lifetime for the S_1 excited state, about 30 fs, as compared to about 400 fs for azobenzene. However, we find that the complete isomerizations have approximately the same time scales. Although the bridging feature in *trans*-B-Ab does not hinder rotation around the NN bond in step 1, it makes twisting of the two phenyl rings around the CN bonds much slower in step 2.

1. Introduction

Azobenzene has been widely studied both experimentally^{1–8} and theoretically,^{9–17} because of its potential applications in molecular switches and other devices. Recently, there has been increasing interest in certain azobenzene derivatives,^{3,5,18–27} because of their novel properties and potential applications.

2,19-Dithia[3.3](4,4′)-diphenyldiazeno(2)phane (Ab-D-1) and 3,3′-bis(1,10-diaza-4,7,13,16-tetraoxa-18-crown-6-carbonyl)-*trans*-azobenzene (Ab-D-2), are two experimentally^{3,5,18–20} and theoretically^{21,22} well-studied azobenzene derivatives. For Ab-D-1, although the rotation around the NN bond was presumably blocked with a cyclophane structure, Rau et al.³ still observed *cis*–*trans* isomerization. The quantum yield with $n\pi^*$ excitation was found to be 24%, close to the 21% yield with $\pi\pi^*$ excitation. On the basis of this experiment, Rau et al. suggested that azobenzene molecules isomerize through rotation around the NN bond if excited to the S_2 state but through CNN angle inversion if excited to S_1 . With femtosecond fluorescence up-conversion spectroscopy, Lu et al.²⁰ investigated the ultrafast relaxation dynamics of three azobenzene derivatives (one of which is Ab-D-1) and found that direct rotation in the S_2 state was unfavorable. On the other hand, in theoretical studies with a semi-empirical reparameterized quantum-mechanical/molecular-mechanical Hamiltonian and a semi-classical surface-hopping approach, Ciminelli et al.²¹ found that photoisomerization of Ab-D-1 for $n\pi^*$ and $\pi\pi^*$ excitations both mainly involved rotation around the NN double bond.

For Ab-D-2, in which azobenzene is capped by an azacrown ether, further evidence for rotation in the S_2 state and inversion in the S_1 state were presented by Rau et al.⁵ Their suggestions were supported by Lednev et al.^{6,18} and Pancur et al.,¹⁹ through ultrafast time-resolved electronic absorption spectroscopy and femtosecond fluorescence up-conversion spectroscopy, respectively. In contrast to these experimental findings, Nonnenberg et al.²² performed first-principles dynamical simulations and found a pathway involving rotation around the NN bond when Ab-D-2 was excited to the S_1 state.

As can be seen from the above history, the mechanisms behind azobenzene photoisomerization appear to be even less well-established when the molecule is sterically hindered by chemical modifications.

There is compelling motivation for trying to achieve better understanding of these mechanisms, because recent work has demonstrated strong advantages of certain bridged azobenzene derivatives for various applications. One such molecule was shown by Haberhauer et al.²⁶ to be a good candidate for prospective novel switching processes, where chirality of the switched states plays an important role. Another bridged azobenzene derivative, 5,6-dihydrodibenzo[*c,g*][1,2]diazocine (B-Ab), has been known for more than 100 years but attracted relatively little attention^{28–31} until very recently, when its high potential as a molecular photoswitch was discovered by Siewertsen et al.²⁷ This group found that the quantum yields for both the *trans*–*cis* and *cis*–*trans* isomerizations of B-Ab are much larger than those of azobenzene. In contrast to nearly coincident $n\pi^*$ absorption bands for *trans*- and *cis*-azobenzene, the corresponding bands are well-resolved for B-Ab, making its *trans*–*cis* and *cis*–*trans* isomerizations reversible with visible light.²⁷ Through *ab initio* molecular dynamics simulations, together with Tully's surface hopping method,³² Böck-

* To whom correspondence should be addressed. E-mail: allen@tamu.edu.

[†] Xi'an Jiaotong University.

[‡] Texas A&M University.

[§] Hubei University.

mann et al.³³ found that the lifetime of the S_1 excited state in *trans*-B-Ab is much shorter than that in *trans*-azobenzene, in addition to the quantum yield being higher.

In the present paper, density-functional-based molecular dynamics simulations are employed to study and compare the *trans*–*cis* isomerizations of azobenzene and B-Ab induced by $n\pi^*$ electronic excitation. The results are consistent with recent experimental²⁷ and theoretical³³ results, in that (i) the quantum yield of *trans*-B-Ab is larger than that of *trans*-azobenzene, (ii) the lifetime of the S_1 excited state is much shorter in *trans*-B-Ab than in *trans*-azobenzene, and (iii) the bridging feature in *trans*-B-Ab does not hinder the rotation around the NN bond.

However, our calculations reveal that the bridging part of the molecule slows the twisting of the two phenyl rings about the CN bonds during the isomerization process. As a result, we find that the time scale for the complete *trans*–*cis* isomerization of this bridged azobenzene is hundreds of femtoseconds and, thus, approximately the same as in azobenzene.

2. Methodology

Detailed descriptions of our method have been published elsewhere.^{34,35} The electronic states are obtained by solving the time-dependent Schrödinger equation in a non-orthogonal basis set, with a time step of 10 as:

$$i\hbar\partial\psi(t)/\partial t = S^{-1}H\psi(t) \quad (1)$$

The Hamiltonian matrix H and overlap matrix S are obtained from the density-functional-based parametrizations of Frauenheim and co-workers.^{36,37} The motion of the nuclei is treated with a generalized Ehrenfest's theorem³⁸

$$M_i \frac{d^2 \mathbf{X}_i}{dt^2} = -\frac{1}{2} \sum_n \psi_n^* \left(\frac{\partial H}{\partial \mathbf{X}_i} - i\hbar \frac{\partial S}{\partial \mathbf{X}_i} \frac{\partial}{\partial t} \right) \psi_n + hc - \frac{\partial U_{\text{rep}}}{\partial \mathbf{X}_i} \quad (2)$$

and the velocity Verlet algorithm³⁹

$$\mathbf{X}_i(t + \Delta t) = \mathbf{X}_i(t) + \dot{\mathbf{X}}_i(t)\Delta t + \frac{1}{2}\ddot{\mathbf{X}}_i(t)(\Delta t)^2 \quad (3)$$

$$\dot{\mathbf{X}}_i(t + \Delta t) = \dot{\mathbf{X}}_i(t) + \frac{1}{2}[\ddot{\mathbf{X}}_i(t + \Delta t) + \ddot{\mathbf{X}}_i(t)]\Delta t \quad (4)$$

This basic method has been successfully used in previous studies of the nonthermal melting of semiconductors³⁵ and the photoisomerization of butadiene,^{34,40} stilbene,^{41,42} and azobenzene,^{43,44} as well as other photo-induced processes.^{45–47} In the present work, we have made one change in the procedure that should lead to better results for the quantum yields. Whereas, in our previous treatments of photoisomerization, the electrons were automatically excited via coupling to the radiation field, here, we focus exclusively on the $n\pi^*$ excitation, by simply placing an electron in the lowest unoccupied molecular orbital (LUMO) and a hole in the highest occupied molecular orbital (HOMO), essentially as in other excited-state molecular dynamics simulations.^{22,33} However, we still allow de-excitation to occur automatically at an avoided crossing near a conical intersection, because we found that de-excitation was already nearly complete in

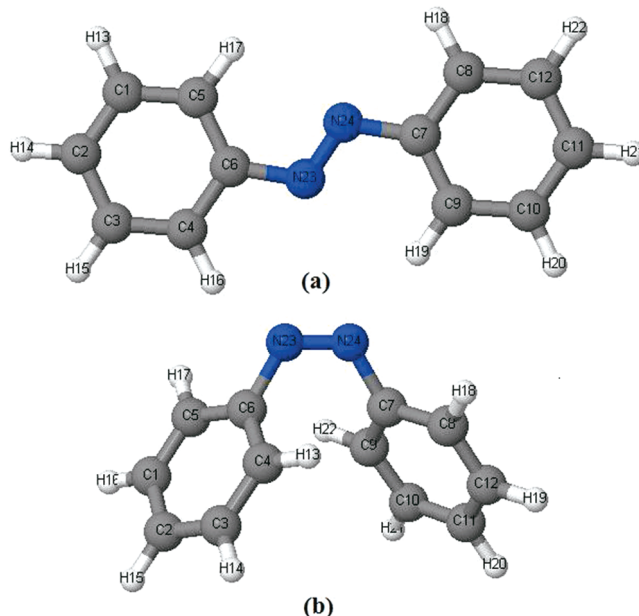


Figure 1. (a) Optimized geometry of *trans*-azobenzene. (b) Optimized geometry of *cis*-azobenzene. All atoms are labeled.

the present simulations, with no need for intervention via, e.g., a surface-hopping scheme.

As described below, 60 non-adiabatic molecular dynamics simulations were performed for *trans*-azobenzene and another 60 for *trans*-B-Ab. The respective quantum yields follow from these full sets of simulations, but the discussions below of the detailed dynamics are based on a single representative simulation for each molecule.

3. Results and Discussion

To obtain the optimized *trans*-azobenzene and *trans*-B-Ab geometries, starting from 300 K, we reduced each nuclear velocity by a factor of 0.9997 after each time step of 0.01 fs, until the total molecular kinetic energy was less than 10^{-7} eV. The optimized geometries are displayed in Figures 1a and 5a. The similarly optimized structures of the corresponding *cis* isomers are shown in Figures 1b and 5b. These structures are in good agreement with the experimental^{27,48,49} and other theoretical^{10,27} results. For azobenzene, the *trans* isomer is 0.25 eV lower in energy than the *cis* form. For B-Ab, on the other hand, the *cis* isomer is more stable than the *trans* isomer, with a 0.39 eV energy difference. Starting from its optimized geometry, each molecule was then heated to 300 K (via random velocities resulting in this temperature) and then allowed to equilibrate and move in the electronic ground state for 2000 fs. The initial conditions for the various simulations were then sampled from the configurations during the last half of this 2000 fs interval.

3.1. *trans*–*cis* Isomerization of Azobenzene. On the basis of 60 simulations, we find a quantum yield of 25% for *trans*–*cis* isomerization of azobenzene induced by $n\pi^*$ excitation. This value is in good agreement with experiment.^{2,5}

We now turn to a detailed discussion of the isomerization process in a single representative simulation. In Figure 2, the molecule is excited to the S_1 state at time $t = 0$. For the 400 fs prior to excitation, while the molecule is in the electronic ground state S_0 but at 300 K, one can observe vibrations of the central CNNC dihedral angle (labeled C6N23N24C7 according to the scheme of Figure 1) around its optimized value of -180° . After

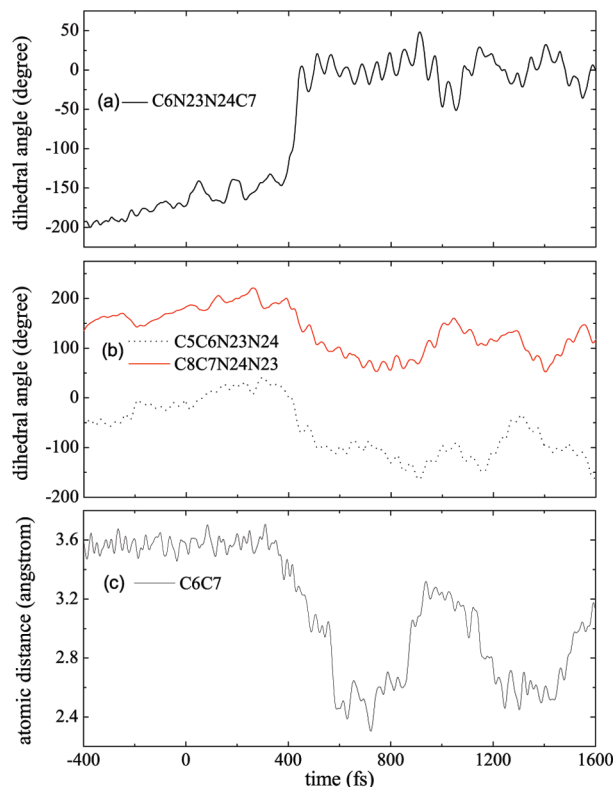


Figure 2. Time dependence in azobenzene of (a) central CNNC dihedral angle, (b) two side CCNN dihedral angles, and (c) C6C7 atomic distance.

the $n\pi^*$ electronic excitation at $t = 0$, it increases to about 7° and then vibrates around this new value. Another two dihedral angles, C5C6N23N24 and C8C7N24N23, are also shown in Figure 2. Before electronic excitation, these CCNN angles vibrate around 180° and 0° , respectively. However, at about 500 fs, both arrive at their respective values in *cis*-azobenzene and then vibrate around them until the end of the simulation. The final graph in Figure 2c shows the distance between the two carbon atoms labeled C6 and C7, which again demonstrates that the molecule arrives at its *cis* geometry in about 500 fs.

The four orbital energies nearest the initial HOMO–LUMO gap are displayed in Figure 3a, and one can see that only the HOMO and LUMO energies themselves are strongly affected by the nuclear motion. The gap between these energies decreases quickly after excitation, first from 2.6 to 1.2 eV and then, after 400 fs, to only 0.01 eV at an avoided crossing where there is a nearly complete de-excitation; i.e., the probability amplitude for a return to the ground state is nearly equal to 1. The lifetime of the S_1 excited state is thus about 400 fs, which agrees well with the experimental value of 340 fs.⁸

The value of the CNNC dihedral angle at the avoided crossing is about 100° , which is consistent with theoretical values near 90° found for the S_1/S_0 conical interaction.^{9,11,13,15} The two CCNN dihedral angles in Figure 2b both vibrate around their initial values (near 0° and 180°) until after 400 fs; i.e., during rotation around the NN bond, both phenyl rings keep a planar orientation with this bond until de-excitation near the S_1/S_0 conical intersection.

The central NN bond, labeled N23N24 in Figure 4, is weakened by excitation, increasing from 1.25 to 1.37 Å and then returning after de-excitation to 1.24 Å. The two neighboring CN bonds, on the other hand, are shortened from 1.46 to 1.3 Å, also returning after de-excitation to their initial values. To

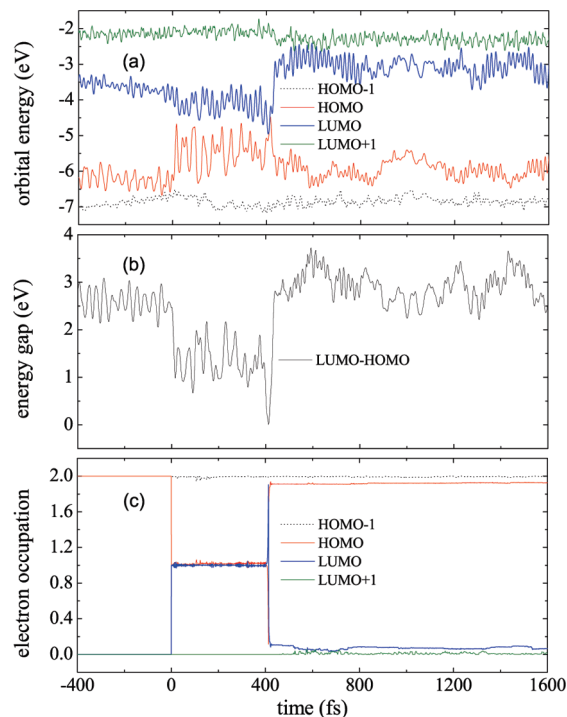


Figure 3. For azobenzene, (a) orbital energies of HOMO – 1, HOMO, LUMO, and LUMO + 1, (b) HOMO–LUMO energy gap, and (c) electron occupancies from HOMO – 1 to LUMO + 1.

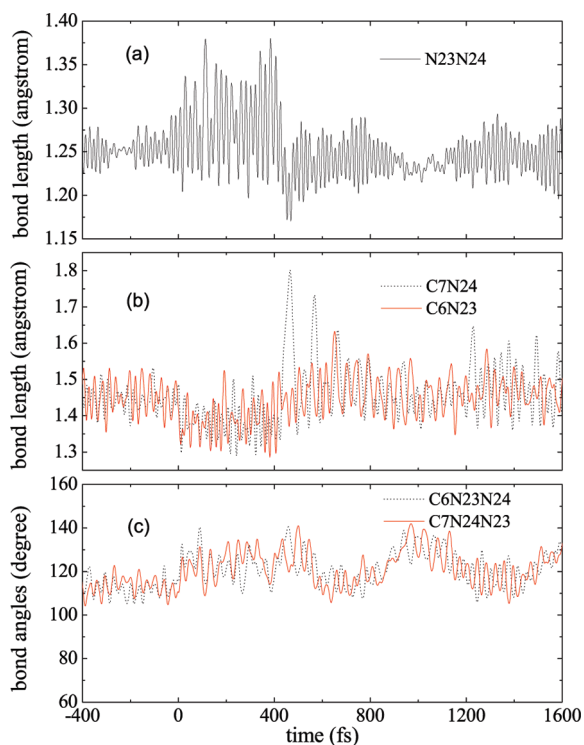


Figure 4. Time dependence (in azobenzene) of (a) central NN bond, (b) two CN bond lengths, and (c) two CNN bond angles.

address the issue of inversion versus rotation as the isomerization mechanism, the two CNN bond angles (C6N23N24 and C7N24N23) are displayed in Figure 4c. They vibrate around 110° in *trans*-azobenzene and 123° in *cis*-azobenzene. Their values during the whole simulation remain far away from 180° ; therefore, inversion involving these angles is not the dominant mechanism in *trans*–*cis* isomerization of azobenzene induced by $n\pi^*$ excitation.

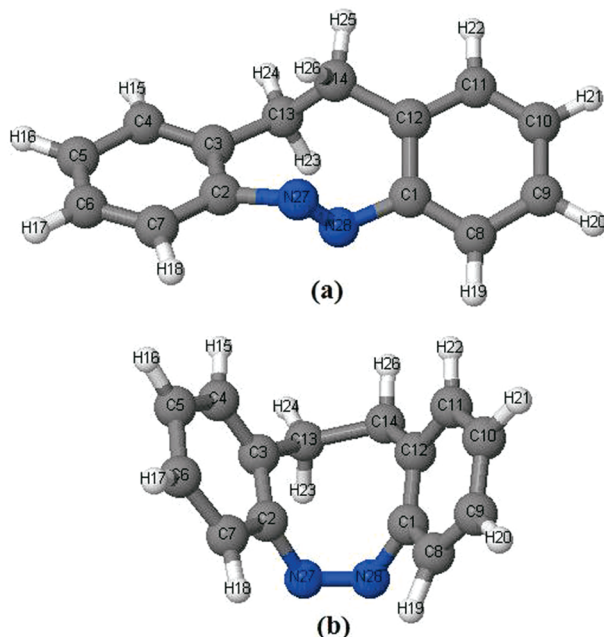


Figure 5. (a) Optimized geometry of *trans*-B-Ab. (b) Optimized geometry of *cis*-B-Ab. All atoms are labeled.

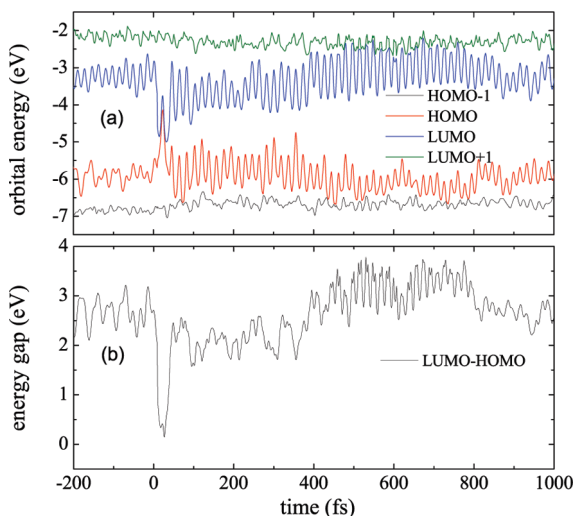


Figure 6. Time dependence in B-Ab of (a) orbital energies from HOMO – 1 to LUMO + 1 and (b) HOMO–LUMO energy gap.

Let us summarize the results presented above. The lifetime of the S_1 state of *trans*-azobenzene is about 400 fs. The whole *trans*–*cis* isomerization process is finished at about 500 fs, with less than 100 fs needed to move from the geometry near the S_1/S_0 conical intersection to the final *cis* geometry. Rotation around the central NN bond is the dominant reaction mechanism, in agreement with previous studies.^{9,10,13,17}

3.2. *trans*–*cis* Isomerization of B-Ab. On the basis of 60 simulations, we find a quantum yield of 45% for *trans*–*cis* isomerization of B-Ab induced by $n\pi^*$ excitation. This result is consistent with the experimental value of $50 \pm 10\%$ obtained by Siewertsen et al.²⁷ and is much larger than the yields for azobenzene in our simulations and experiment.^{2,5}

Again, we show detailed results from a single representative simulation, with the orbital energies from HOMO – 1 to LUMO + 1 displayed in Figure 6a and the HOMO–LUMO gap in Figure 6b. The molecule is again initially in the electronic ground state, undergoing $n\pi^*$ excitation at $t = 0$. As the nuclei move in response to the resulting Hellmann–Feynman forces,

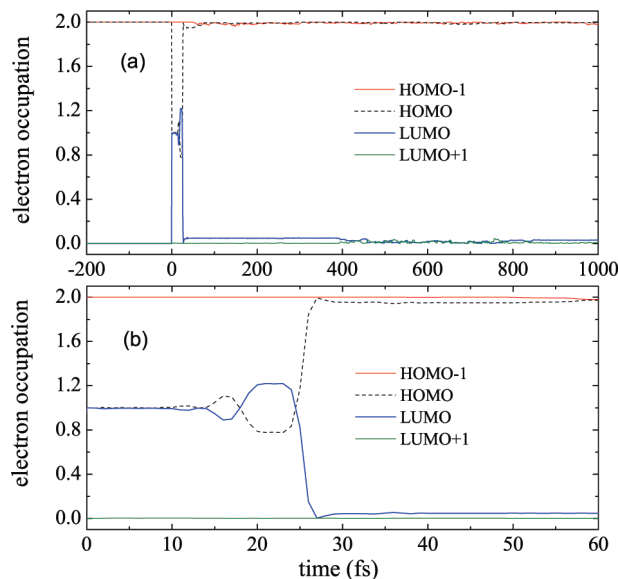


Figure 7. (a) Electron occupancies in B-Ab from HOMO – 1 to LUMO + 1. (b) Details of Figure 5a from 0 to 60 fs.

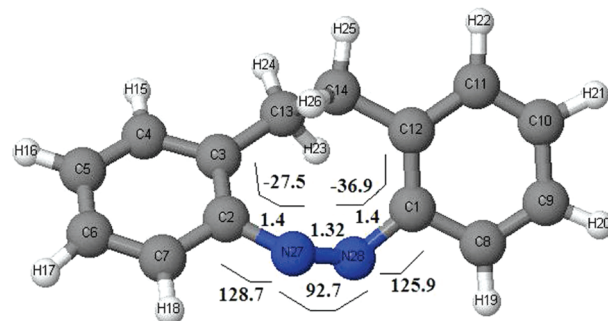


Figure 8. Geometry of B-Ab at 25 fs in our simulation, which is near a S_1/S_0 conical intersection. Bond lengths are in angstroms, and bond angles and dihedral angles are in degrees.

the energy gap between HOMO and LUMO then decreases dramatically, reaching 0.15 eV for $t = 25$ fs (at an avoided crossing near the S_1/S_0 conical intersection, as discussed below). It then increases to 2.0 eV at 45 fs and 3.3 eV at 430 fs.

The electron occupancies for the four states of Figure 6a are shown in Figure 7. Notice that the electron in the LUMO undergoes a nearly complete transition to the HOMO between 25 and 27 fs; i.e., the probability amplitude is nearly equal to 1 for the B-Ab molecule to be in its ground state after 27 fs, and the lifetime of the S_1 excited state for *trans*-B-Ab is thus found to be below 30 fs.

The geometry of the B-Ab molecule at $t = 25$ fs is shown in Figure 8. At this point, the central CNNC dihedral angle is equal to 92.7° , near the value corresponding to the S_1/S_0 conical intersection geometry of azobenzene.^{9,10,13} Both the CNN bond angles (with values of 128.7° and 125.9° for C2N27N28 and C1N28N27, respectively) are far away from 180° that would correspond to inversion. The two CCNN dihedral angles (labeled C3C2N27N28 and C12C2N28N27 in Figure 5) are equal to -27.5° and -36.9° , respectively. Because the two phenyl rings have undergone some twisting around the CN bonds, these angles are larger than their initial values in *trans*-B-Ab (about -65°) but are still far away from their corresponding values in *cis*-B-Ab.

The time dependence of the central NN (N27N28) bond length is shown in Figure 9a. After electronic excitation, its value (averaged over vibrations) increases from 1.24 to 1.41 Å

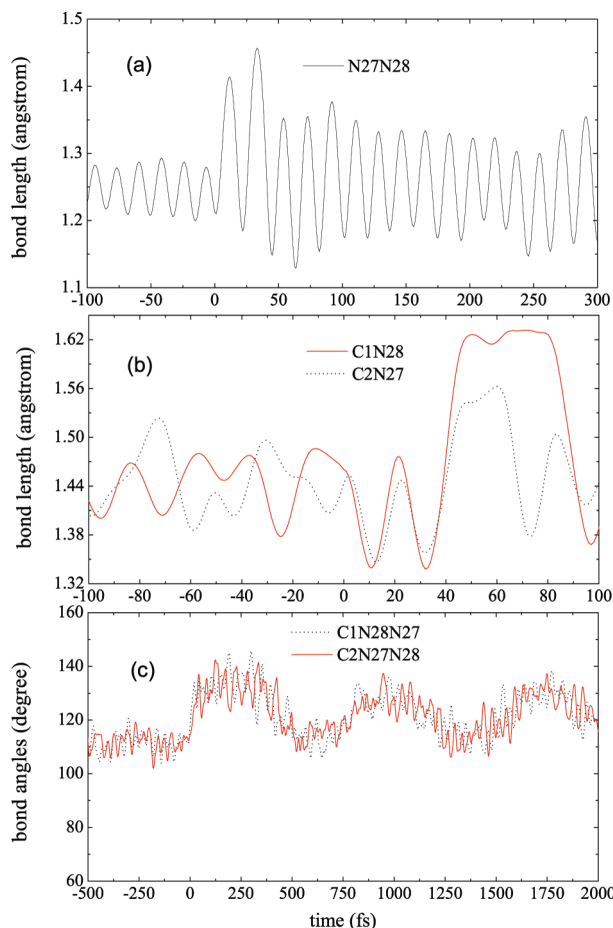


Figure 9. Time dependence in B-Ab of (a) NN bond length, (b) two CN bond lengths, and (c) two CNN bond angles.

very quickly, returning to its initial value after de-excitation. The lengths of the two central CN bonds (C1N28 and C2N27), shown in Figure 9b, are shortened from 1.44 to 1.34 Å after excitation but also return to their initial values following de-excitation. The $n\pi^*$ electronic excitation also weakens the NN bond while tightening the neighboring CN bonds. Therefore, the basic behavior of the states near the HOMO–LUMO gap are unaffected by the bridging feature in the molecule, and the same is true of the mechanism of isomerization.

However, rotation about the central NN bond proceeds far more rapidly in the bridged molecule, as seen in Figure 10 and as also found in ref 33. The time dependence of the central dihedral angle is displayed in Figure 10a, with the optimized value in *cis*-B-Ab (5.2°) also shown for comparison. Immediately after excitation, this angle rapidly decreases. At 25 fs, it reaches 93° (near the S_1/S_0 conical intersection for B-Ab, as explained above), and at 45 fs, it already has attained its final value in the *cis* isomer. However, the isomerization process is not really completed at this point, because the phenyl rings lag behind, as seen in Figure 10b, where the two central CCNN dihedral angles are plotted and compared to their optimized values in the *cis* structure. Another dihedral angle in the bridge ring, C3C13C14C12, is also plotted in Figure 10c and confirms that isomerization is not finished at 45 fs. The two phenyl rings continue to twist around the CN bonds after B-Ab has returned to the electronic ground state, with *trans*–*cis* isomerization finally completed at about 430 fs.

The lifetime of the S_1 excited state for *trans*-B-Ab is about 30 fs, which is an order of magnitude shorter than the *trans*-azobenzene lifetime (400 fs). This same conclusion was

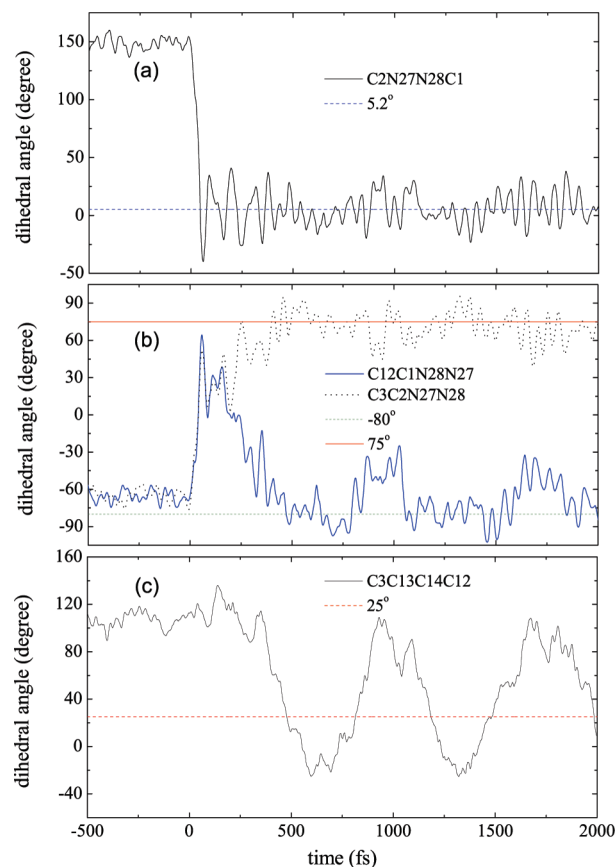


Figure 10. Time dependence in B-Ab of (a) CNNC dihedral angle, where 5.2° is the optimized value in *cis*-B-Ab, (b) C12C1N28N27 and C3C2N27N28 dihedral angles, where -80° and 75° , respectively, are the optimized values in *cis*-B-Ab, and (c) C3C13C14C12 dihedral angle of the bridge structure in B-Ab, where 25° is the optimized value in *cis*-B-Ab.

previously reached by Böckmann et al.³³ Our results also confirm the previous conclusions by Nonnenberg et al.²² that rotation rather than inversion is the mechanism for isomerization and that the bridge ring does not hinder rotation around the NN bond.

There are two stages in the isomerization process, with B-Ab completing the first much more rapidly but the second much more slowly (in comparison to bare azobenzene). (1) Upon excitation, the lower symmetry of B-Ab results in Hellmann–Feynman forces, which immediately act to initiate rotation around the central NN bond, as can be seen in a comparison of Figure 10a to Figure 2a near $t = 0$. There is then a very rapid approach to an avoided crossing near the conical intersection, where the molecule undergoes a transition from S_1 to S_0 within 2 fs, and a further rapid movement onward to the final value of the CNNC dihedral angle in the *cis* geometry. (2) In the second stage, however, the twisting of the phenyl rings in B-Ab around the CN bonds is hindered by the presence of the bridge structure ($-\text{CH}_2-\text{CH}_2-$). Therefore, this stage is required much longer for B-Ab (about 400 fs) than for simple azobenzene (about 70 fs).

4. Conclusions

Density-functional-based molecular dynamics simulations were performed for isomerization of azobenzene and bridged azobenzene induced by $n\pi^*$ excitation. The quantum yield was found to be about 25% for azobenzene, in agreement with experiment,^{2,5} and about 45% for bridged azobenzene, which is

again consistent with experiment.²⁷ In those simulations that did produce isomerization, the range of calculated S₁ lifetimes was 330–480 fs for azobenzene and 22–32 fs for bridged azobenzene.

In the simulation shown in detail, the lifetime of the S₁ excited state in *trans*-azobenzene was found to be about 400 fs, with the whole *trans*–*cis* isomerization process completed in approximately 500 fs. The S₁ lifetime in *trans*-B-Ab was found to be only about 30 fs, an order of magnitude shorter, just as in the earlier work by Böckmann et al.³³ However, the full *trans*–*cis* isomerization for B-Ab requires about 430 fs, which is comparable to the time scale for azobenzene. The reason for this is that the twisting of the phenyl rings in B-Ab around the CN bonds is hindered by the presence of the bridge structure.

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