

Photoisomerization of Azobenzene

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Abstract

It has been found by experiment that geometric isomers of azobenzene derivatives can be switched by UV-Visible irradiation. When included with cyclodextrin, the complex could be made as a light-driven molecular shuttle, a piece of molecular machines. Of course, the movement of the shuttle is forced by the photoisomerization of the azobenzenes. However, the mechanism for the process is still unclear. Recently, semi-empirical calculations have been carried out to study the conformation isomerization of the ground state of an azobenzene derivative. The calculations revealed a huge barrier of more than 50 kcal/mol between the cis and the trans forms. In this study, geometry optimizations and energy evaluations were performed for the ground state (S₀), the 1st excited state (S₁), and the 2nd excited state (S₂) of various conformations of azobenzene, the parent compound of the azobenzene derivatives, using *ab initio* calculations. For S₀, the HF/6-31G* and MP2/6-31G*/HF/6-31G* were employed whereas the CIS/6-31G* were used for S₁ and S₂. The potential energy curves for the conformational isomerization of the 3 states were then plotted.

1. Introduction

Molecular shuttles are an important part of molecular machines and nanotechnology. This nanodevice can be made as a molecular switch for the molecular-scale integrated circuit. The shuttle could be driven by several mechanisms such as thermal and pH of solutions.[1] Recently, Murakami and coworkers [2] has succeeded in producing a light-driven molecular shuttle based on the supramolecular compound of α -cyclodextrin and the derivative of azobenzene. The mechanism triggers by the transformation of the cis and the trans isomers of the azobenzene derivative. The trans isomer could be converted to the cis form by irradiating UV light of 360 nm and the reverse transformation (cis \rightarrow trans) is achieved on the irradiation of 430 nm light. It was also reported that the photoisomerization reached the photostationary state within 15 min while the thermal isomerization has the half-life of 13 h at 5 °C and 50 min at 30 °C. This implies that the thermal isomerization is a much slower process. The shuttle mechanism of the Murakami's compound has also been studied using semiempirical AM1 calculations by Sohlberg et.al.[3] However, the article did not investigate on the photoisomerization aspect of the azobenzene derivative. Since azobenzene also exhibits photoisomerization by irradiation of UV light, the theoretical investigation of the photo-isomerization process of azobenzene would help us to understand the light-driven mechanism of the molecular shuttle. In this work, the photoisomerization of azobenzene is studied using combinations of Hartree-Fock (HF) and Configuration Interaction Singles (CIS) methods.

2. Computational Details

Geometries for the ground (S0) and 2 excited states (S1 and S2) of the 3 conformers of azobenzene at CNNC dihedral angle of 0° (cis), 90°, and 180° (trans), see Fig. 1, were optimized at HF/6-31G* (S0 state) and CIS/6-31G* (S1 and S2 states). The MP2/6-31G**//HF/6-31G* energies were calculated for the 3 isomers at S0 state to determine the effect of electron correlation on relative stability of these isomers. For S1 and S2 states, CIS energies of 3 isomers at their corresponding S0 geometries were also computed to estimate the vertical excitations. All calculations were performed using the Gaussian98 program[4] on the SGI Octane2 computer.

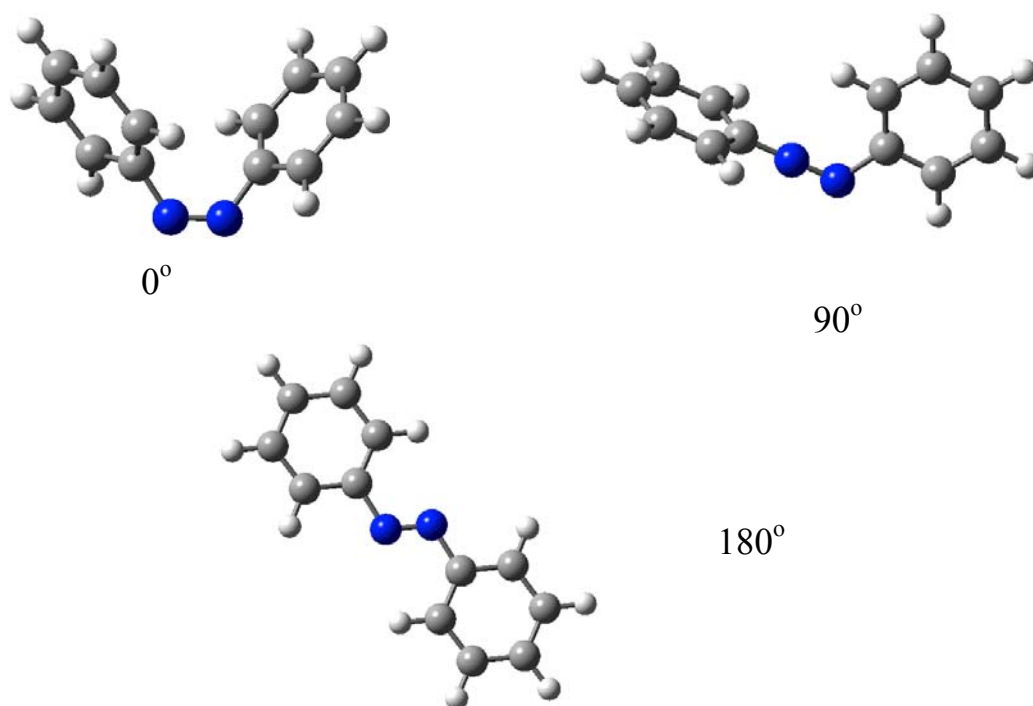


Fig. 1. Three isomers of azobenzene; Carbon is represented by grey color, nitrogen by blue color and hydrogen by white color.

3. Results and Discussion

Selected geometrical parameters of different isomers of azobenzene at 3 different states calculated using HF/6-31G** and CIS/6-31G** were displayed in Table 1. The R(N-N) bond distance and 2 dihedral angles represented the angle between the plane of the phenyl ring and N=N plane were given.

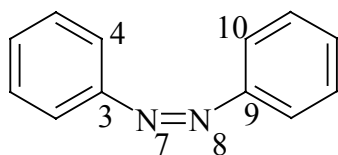


Table 1 Selected geometrical parameters of 3 isomers of azobenzene at S0, S1, and S2 states

isomer	S0	S1	S2
0°			
R(N-N); Å	1.217	1.208	1.288
C4C8N7N8; deg	129.9	153.0	150.3
C10C9N8N7; deg	129.9	153.0	166.0
90°			
R(N-N); Å	1.200	1.236	1.184
C4C8N7N8; deg	180.0	178.0	180.0
C10C9N8N7; deg	-179.6	178.3	179.9
180°			
R(N-N); Å	1.220	1.232	1.317
C4C8N7N8; deg	0.0	0.0	0.0
C10C9N8N7; deg	-179.6	180.0	180.0

The vertical excitations, the energy difference between S0 and Sn at the same geometry, of cis and trans isomer of azobenzene as well as their oscillator strengths were listed in Table 2. These vertical excitations render the irradiation energies. It appears that the S0→S1 transitions of both forms are in the UV region and the cis form absorbs light at the longer wavelength similar to those reported by Murakami. Although a shorter wavelength as compared to Murakami's compound is observed for both cis and trans form, the calculations are remarkably in agreement with Murakami's findings since the shift of the wavelength could be expected for the derivatives. However, the trans form has 0 oscillator strength which implies that the transition would probably not occur while only weak intensity would be observed for the absorption of the cis form. Interestingly, the absorptions for S0→S2 are also in the UV region and have higher oscillator strengths. So it could be possible that the observed transition is S0→S2 rather than S0→S1.

Table 2 Vertical excitations (nm) and oscillator strength (f) between S0 and S1 and S0 and S2 of cis and trans isomers of azobenzene

isomer	S0→S1	f	S0→S2	f
cis (0°)	364.8	0.020	358.8	0.242
trans (180°)	208.4	0.000	245.1	0.909

Table 3 shows relative energies between azobenzene isomers at 3 different states calculated using HF/6-31G**, MP2/6-31G**//HF/6-31G**, and CIS/6-31G**. Table 4 displays the

adiabatic excitations, energy difference between S0 and S_n state at their optimized geometry, calculated using HF/6-31G** and CIS/6-31G**. Table 2, 3, and 4 were summarized in Fig. 2.

Table 3 Relative energies (kcal/mol) between isomers of azobenzene at S0, S1, and S2 states

isomer	S0 (HF)	S0 (MP2)	S1	S2
0°	17.29	11.86	23.58	32.88
90°	49.66	45.56	0.00	73.48
180°	0.00	0.00	4.21	0.00

Table 4 Adiabatic excitations (kcal/mol) between S0 and S1 and S2 states of 3 isomers of azobenzene

isomer	S0→S1	S0→S2
0 _o	66.07	116.38
90 _o	14.32	124.61
180 _o	68.20	100.79

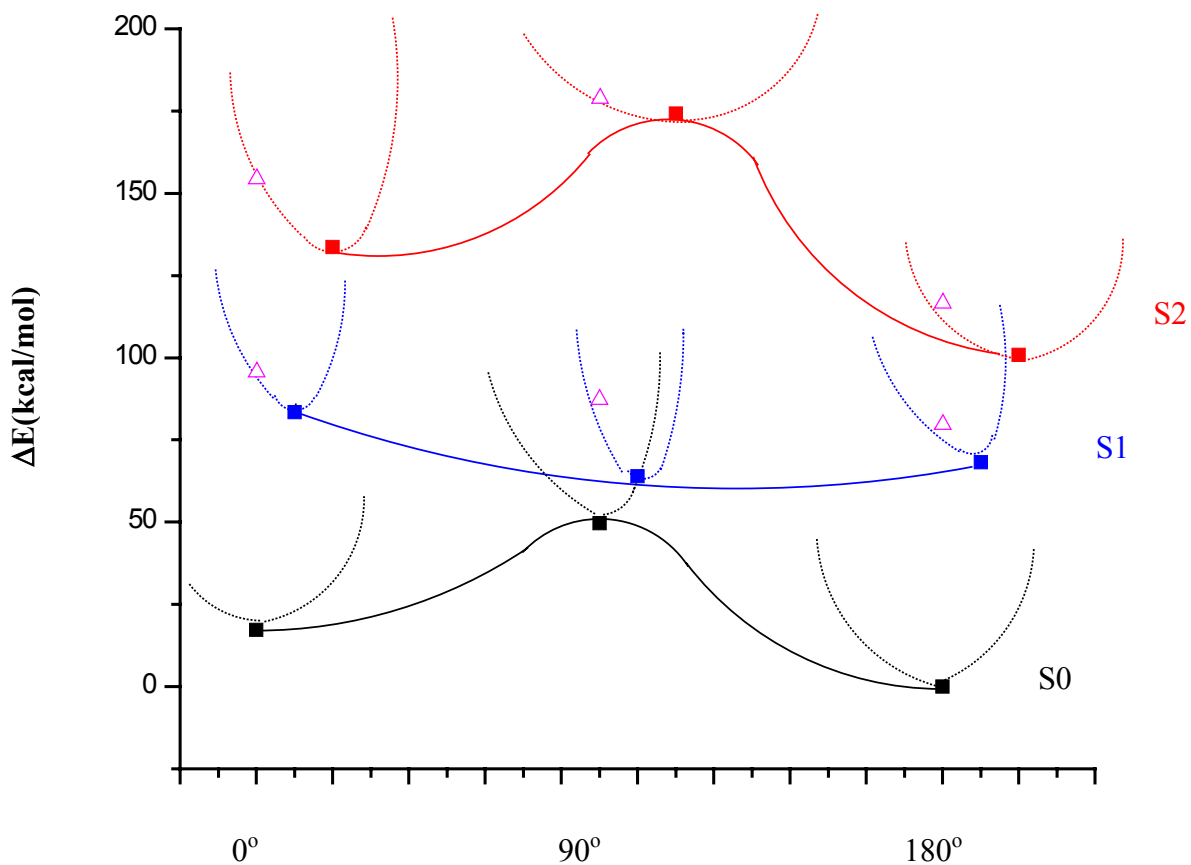


Fig. 2 Torsional potential of azobenzene at S0, S1, and S2 states

In Fig. 2, imaginary lines linked between vertical and adiabatic excitation points are made. These lines represent the approximate vibrational potential of azobenzene isomers at various states. From Fig 2., the photoisomerization process could be explained. At S0, the transformation from trans to cis isomers would require a very high energy since it needs the energy of at least 49.66 kcal/mol to overcome the potential barrier. Thus, the tran-cis isomerization will not occur spontaneously at the room temperature and likewise for the cis-trans isomerization since there exists approximately a 30 kcal/mol barrier. Interestingly, at S1 the potential minimum is at 90° isomer. The excitation at both cis and trans forms will readily put the azobenzene to the 90° conformer. The potential at S2 is, however, similar to at S0 but with the higher potential barrier, 73.48 kcal/mol for trans→cis potential. From this information, we would like to propose the mechanism for photoisomerization of azobenzene. The most stable form of azobenzene is the trans isomer. When the molecule at trans conformer is absorbed light at 208.4 nm, it will be excited to S1. At this point, the molecule is not at the vibrational minimum of the trans at S1 so the molecule will be relaxed. Once it reaches the vibrational minimum, it will transform to the 90° conformer which is the S1 potential minimum. The vibrational 14.32 kcal/mol different (as illustrated in Fig. 2). Therefore, it is very likely that at this point the molecule will be deexcited to S0 through the coupling of the vibrational states of S0 and S1. Now the molecule is at the highest point of the S0 potential (90° isomer), it can be transformed to both trans and cis forms. If it switches over to the cis form, the photoisomerization takes place. Similar process would be obtained for the photoisomerization of cis to trans. The excitation to S2 could not initiate the isomerization because the S2 potential is very to that of S0 and thus high energy would be required. Thus, without light the cis and trans isomerization will not occur at room temperature. However, the stabilization of trans over cis forms for azobenzene may be different from the experimental result of Murakami since for the derivative the steric from the substituents might cause the trans form to become less stable. Moreover, for azobenzene the transition to S1 of the trans conformer would not be possible because of zero oscillator strength is observed (Table 2) but it is also possible that for the derivatives this situation might change. Therefore, we believe that the photoisomerization of azobenzene derivatives could still be described by the proposed mechanism.

4. Conclusion

The photoisomerization of azobenzene is achieved through the stabilization of the 90° isomer at S1 against other isomers. The excited molecule at cis and trans isomer will be readily changed to 90° conformer which in turns will be deexcited to S0 and then relaxed to cis and trans form at S0. The substitution might cause the potential of azobenzene derivatives to be slightly different from those of azobenzene. However, the photoisomerization could still be described by the above procedure.

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