

Molecular Structures of 2,2-Bipyridine and Its Anion Radical: Multiconfiguration-SCF Calculations

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The electronic structures and conformational behaviors of the neutral and anionic 2,2-bipyridine species are investigated with the multiconfiguration-SCF (MCSCF) method. The MCSCF calculations show that the lowest triplet states of neutral molecule and the doublet state of anionic species have the local minimum structures corresponding to the *cis* and trans forms. The MCQDPT2 calculation predicts that the lowest triplet state of the trans form lies 5.3 kcal/mol above the ground singlet state. The best level of theory predicts that the energy of the lowest doublet states of the anion trans and *cis* forms is 1.7 kcal/mol above the neutral singlet state.

Key Words : 2,2-Bipyridine, MCSCF, Open-shell, Triplet state, Doublet state

Introduction

Organic molecules containing π -conjugated system have long been a subject of great interest for wide variety of reasons. Some π -conjugated heterocyclic rings such as azaaromatic molecules have been considered to be a useful tool for designing new materials for advanced applications such as photochemical devices.^{1,2} In particular, 2,2-bipyridine is one of such molecules, well known as a chelating ligand widely used for many transition metal complexes.³⁻⁵ Especially various metal complexes of 2,2-bipyridine have been explored as a potential candidate for solar energy devices, energy storages, and future nonlinear optical materials.⁶⁻⁸ Furthermore, the unique molecular and electronic structures of 2,2-bipyridine in both neutral and anionic forms have been an interesting topic for discussion in spectroscopic and quantum theoretical areas.⁹⁻²⁰

The experimental^{12,13} and theoretical studies^{14,15} on neutral 2,2-bipyridine so far strongly indicate that the ground state has two local minimum structures corresponding to the trans and gauche(twisted) conformations. An experimental study using resonance Raman method reported that the lowest triplet state resulting from $\pi\pi^*$ transition has the trans conformation.¹⁶ A recent study using both resonance Raman spectroscopy and CIS calculations showed an interesting conformational feature of anion radical.²⁰ According to this study, the anionic species do not seem to have a planar structure. This result is in disagreement with previous DFT study by the same research group¹⁹ in which the conformation of anionic species has planar one. Therefore, more intensive study is required because the previous theoretical studies for the open-shell bipyridine systems have not been confirmed by the reasonable multiconfiguration calculations. Specifically, the potential energy surface in terms of dihedral angle of two pyridine rings need to be examined more intensively with the multiconfiguration wavefunction.

It is a well known fact that the unrestricted calculation is crucial for analyzing the electronic structure of radical

systems. Such calculations for open-shell system however become highly complicated due to possible spin contamination from the higher multiplicity states.^{21,22} It is also well known that many open-shell calculation with π conjugated system show the significant multiconfiguration character²³ as well as serious spin contamination and thus cannot be handled by the simple projection method.²⁴ Therefore, the situation like bipyridine system naturally calls for a multiconfigurational approach. Recent dramatic advancements in computer hardware and software make it possible to extend the application of multiconfiguration SCF (MCSCF) method to much larger open-shell molecular systems such as bipyridine. It is the aim of the present study to investigate the structural features in terms of the electronic structures for 2,2-bipyridine and its anion species by using high level *ab initio* multireference calculations.

Computational Details

The molecular structure of the neutral (singlet ground and first triplet states) of 2,2-bipyridine for several possible structures including the *cis*, gauche(twisted), and trans conformations were optimized at the fully optimized reaction space (FORS)-MCSCF²⁵ level with the 6-31G(d) basis set. The geometry optimizations for the *cis*, gauche, and trans conformations were restricted to the C_{2v}, C₂ and C_{2h} point group, respectively. The active space in our MCSCF geometry optimization for the ground and triplet states can be denoted as (12, 12) which includes all π electrons and orbitals in this system. According to our test calculations with the (16, 14) active space including all π as well as the nitrogen nonbonding systems, addition of the nitrogen nonbonding orbitals barely affects the electronic structures involving $\pi\pi^*$ transition in this system. That is, the MCSCF (12, 12) calculations are pretty safe for examining the nature of electronic states corresponding to the structural change of π systems.

In case of anion species with the doublet state, the (13, 12)

active space were used for all MCSCF geometry optimization as well as the potential energy surface scan. The MCSCF Hessian calculations for all neutral and anionic species were carried out with the 6-31G(d) basis set to determine whether optimized structures are local minimum. In order to achieve a more reliable energy comparison among the electronic states, a MCQDPT²⁶ single point energy corrections were performed with the 6-31G(d) and 6-311+G(d) basis sets. All calculation was performed using the GAMESS²⁷ electronic structure program.

Results and Discussion

Molecular Structures and Conformations. Figure 1 shows the chemical structure of 2,2-bipyridine system with atomic numbering. According to the previous experiments and theoretical studies based on the single reference wavefunction calculation, the neutral 2,2-bipyridine molecules appear to have two local minima corresponding to the trans and twisted (gauche) conformations on the energy hypersurface.^{14,15} In addition, the lowest triplet state corresponding to the $\pi\pi^*$ transition seems to have the trans conformation with the N₂-C₁-C_{1'}-N_{2'} dihedral angle of 180°. Our MCSCF geometry optimizations are quite consistent with these conclusions for the singlet ground state of the neutral species. However, the present MCSCF calculations for the lowest triplet state suggests that both the trans and *cis* conformations are the local minima on the potential energy surface in which the trans form is the global energy minimum structure.

The molecular structures of the lowest electronic states for the neutral and anionic 2,2-bipyridine are summarized in Table 1. In this table, there are no remarkable structural differences between the two different conformations in both ground and triplet states except for the N₂-C₁-C_{1'}-N_{2'} dihedral angle. It is obvious that the triplet $\pi\pi^*$ transition shortens the C₁-C_{1'} bond lengths. In both trans and *cis* forms, the triplet C₁-C_{1'} bond lengths are about 0.1 Å shorter than those of the ground state. The bond length shortenings in triplet transition are also found in the N₂-C₃ and C₅-C₆ bonds. These bond length changes between the singlet and triplet states are well related to the changes of NOON (natural orbital occupation number) values²³ of two active spaces illustrated in Figure 2. In singlet ground state with trans form, the NOONs of b_g and a_u orbitals are close to 2 and 0, respectively. The NOONs of both two active spaces however approach to about unity in the triplet state. This change suggests that some bondings associated with b_g orbital get longer in triplet state, while some bondings

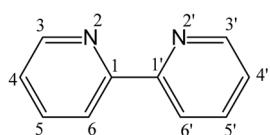


Figure 1. Chemical structure of 2,2-bipyridine with atomic numbering.

Table 1. Geometric parameters of the lowest electronic states for the neutral and anionic species of 2,2-bipyridine. (Distances, Å; Angles, deg)

Geometric Parameters	Neutral/Singlet ^a		Neutral/Triplet ^a		Anion/Doublet ^b	
	gauche	trans	<i>cis</i>	trans	<i>cis</i>	trans
	¹ A	¹ A _g	³ B ₂	³ B _u	² B ₁	² A _u
C ₁ -C _{1'}	1.494	1.491	1.395	1.390	1.425	1.420
C ₁ -N ₂	1.335	1.335	1.397	1.398	1.374	1.372
N ₂ -C ₃	1.329	1.330	1.297	1.299	1.318	1.324
C ₃ -C ₄	1.396	1.393	1.436	1.434	1.400	1.394
C ₄ -C ₅	1.392	1.394	1.410	1.414	1.412	1.418
C ₅ -C ₆	1.393	1.391	1.375	1.373	1.374	1.372
C ₁ -C ₆	1.400	1.402	1.463	1.459	1.440	1.438
∠N ₂ -C ₁ -C ₆	122.1	122.1	119.2	120.2	118.2	119.3
∠C ₃ -N ₂ -C ₁	118.5	118.8	119.2	118.7	119.4	118.8
∠C ₄ -C ₃ -N ₂	123.6	123.4	124.7	124.4	125.9	125.6
∠C ₅ -C ₄ -C ₃	118.1	118.1	117.6	118.0	116.0	116.4
∠C ₄ -C ₅ -C ₆	118.5	118.9	119.2	119.2	119.6	119.5
∠C ₅ -C ₆ -C ₁	119.2	118.8	120.1	119.5	121.0	120.4
D(N ₂ -C ₁ -C _{1'} -N _{2'})	43.3	180.0	0.0	180.0	0.0	180.0

^aMCSCF(12,12)/6-31G(d) level. ^bMCSCF(13,12)/6-31G(d) level.

associated with a_u orbital are shortened. The C₄-C₃-N₂ bond angles of both singlet and triplet states are deviated notably from the value of sp² hybrid orbital. The MCSCF calculation estimates the N₂-C₁-C_{1'}-N_{2'} dihedral angle of the singlet gauche conformer at about 43°. Our MCSCF geometry optimizations also estimates the triplet state resulting from $\pi\pi^*$ transition to be both *cis* (N₂-C₁-C_{1'}-N_{2'} dihedral angle = 0°) and trans (N₂-C₁-C_{1'}-N_{2'} dihedral angle = 180°) conformations, as discussed above.

The molecular structures of anionic species are also notably different from the neutral one. As can be seen in Table 1, the anionic C₁-C_{1'}, N₂-C₃ and C₅-C₆ bondings are shorter than those of neutral ones, while other anionic bondings are longer than those of neutral ones. This seems due to the fact that the contribution of the molecular orbital with a_u symmetry increases in the anionic species. (See Figure 2.) In case of the trans conformation, when an extra electron is added onto an orbital with a_u symmetry in anionic species, some bondings overlapped with the electron density of this orbital is shortened, while other bondings is lengthened. Overall trend of bond angle changes is pretty similar to the triplet species.

The conformational behavior of anionic species is a subject of some interest. The previous DFT study¹⁹ reports the conformation of anionic species has planar structure. How-

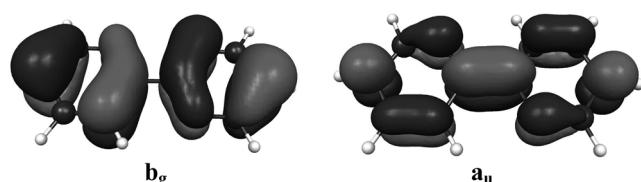


Figure 2. Two active spaces with b_g (left) and a_u (right) symmetry of trans 2,2-bipyridine.

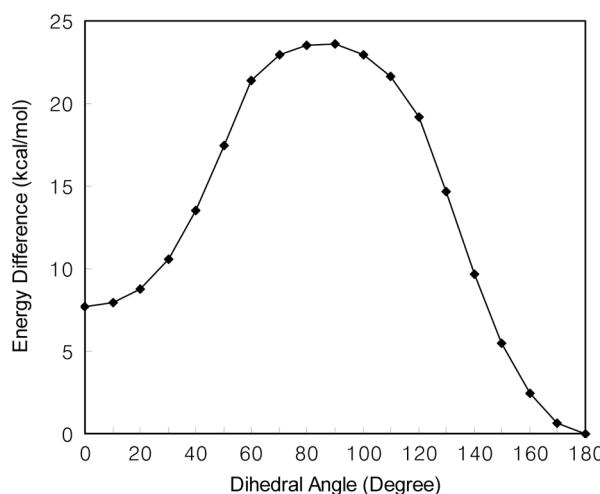


Figure 3. Potential energy curve of anionic 2,2-bipyridine with respect to $N_2-C_1-C_1-N_2$ dihedral angle at the MCSCF(13, 12)/6-31G(d) level of theory.

ever, the recent study²⁰ suggests that the conformation of anionic species is the gauche form with C_2 symmetry somewhat twisted from the trans form. The present study concludes that both the trans and *cis* conformations are stable in the anionic species. According to our MCSCF (13, 12) potential energy surface scan, it is obvious that there are only two local minimum points corresponding to the *cis* and trans conformations. (See Figure 3) Figure 3 shows that the MCSCF energy barrier for change from *cis* to trans is about 15 kcal/mol. This value increases up to about 20 kcal/mol at the MCQDPT2 level. Of course, it is possible that the solvent effect in the resonance Raman experiment in liquid phase disturbs the conformation of anionic species. Nevertheless, more intensive experimental study should be necessary to verify the nature of conformation of anionic 2,2-bipyridine.

Relative Energies. The relative energies between some electronic states for neutral and anionic species of 2,2-bipyridine are summarized in Table 2. It is confirmed once again that the trans form is the global minimum in the

neutral singlet species. The twisted form (gauche) lies about 6.3 kcal/mol above the trans form at the MCSCF level. The MCQDPT2/6-311+G(d) calculations estimates this energy difference to be about 5.3 kcal/mol. In triplet species, the trans form is also more favorable than the *cis* form. The lowest triplet state of trans conformation (3B_u) lies about 66 kcal/mol above the singlet state. The next triplet state (3A_g) of trans form lies about 24 kcal/mol above the 3B_u state. The energies of triplet states of *cis* form (3B_2 and 3A_1) are about 10 kcal/mol higher than the trans one.

As explained above, the anionic species also has two local minima corresponding to *cis* and trans conformations. The ground state of anionic species with the trans form is 2A_u , whereas the *cis* form has the ground state of 2B_1 . The relative energies of anionic species are clearly very sensitive to both basis set and level of theory. It is natural that a diffuse function and dynamic correlation are required for an adequate assessment of this anionic species. At the best level of theory, MCQDPT2 with the 6-311+G(d) basis set, the energy of lowest doublet states of trans form (2A_u) is 1.7 kcal/mol higher than the neutral singlet one. Indeed, this value can be considered as an electron affinity of 2,2-bipyridine. The doublet *cis* form (2B_1) lies at least 8 kcal/mol above the trans form at the same level of theory. The next doublet state of trans form (2B_g) is predicted to be about 14 kcal/mol higher in energy than the 2A_u , whereas the 2A_2 state of *cis* form is about 24 kcal/mol higher than the 2B_1 state.

Conclusions

The electronic structures and conformational behaviors of the neutral and anionic 2,2-bipyridine species are investigated with the multiconfiguration-SCF (MCSCF) method. It turns out that the lowest triplet state resulting from $\pi\pi^*$ transition has two local minimum structures corresponding to the *cis* and trans conformations, whereas the ground singlet state has both twisted (gauche) and trans conformations. The structural changes in triplet states are well consistent with the changes NOONs of MCSCF calculations. In addition, it is suggested that the anionic species

Table 2. Relative energies (kcal/mol) between some electronic states for neutral and anionic species of 2,2-bipyridine

Theoretical Level		MCSCF/ 6-31G(d)	MCSCF/ 6-311+G(d) ^a	MCQDPT2/ 6-31G(d) ^b	MCQDPT2/ 6-311+G(d) ^c
Anion/ Doublet ^d	<i>cis</i>	2A_2	91.3	53.1	81.7
		2B_1	54.7	25.8	46.5
	<i>trans</i>	2B_g	71.9	35.2	61.1
		2A_u	47.0	17.5	38.9
Neutral/ Triplet	<i>cis</i>	3A_1	101.2	103.4	100.9
		3B_2	76.2	77.3	75.7
	<i>trans</i>	3A_g	92.1	93.4	91.9
		3B_u	68.4	68.9	68.1
Neutral/ Singlet	gauche	1A	6.3	6.4	5.9
	<i>trans</i>	1A_g	0.0	0.0	0.0

^aMCSCF(12,12)/6-311+G(d)//MCSCF(12,12)/6-31G(d) level. ^bMCQDPT2(12,12)/6-31G(d)//MCSCF(12,12)/6-31G(d) level. ^cMCQDPT2(12,12)/6-311+G(d)//MCSCF(12,12)/6-31G(d) level. ^d(13, 12) active space is used for anion species.

also has both *cis* and trans conformations. The MCSCF potential energy surface scan confirms that there is no local minimum point corresponding to the twisted (gauche) form which was suggested from the previous experimental study.

The MCQDPT2 calculation predicts that the lowest triplet state of trans form lies at 5.3 kcal/mol above the ground singlet state. The triplet state of *cis* form is located at about 10 kcal/mol higher in energy than that of trans one. It turns out that the diffuse function and dynamic correlation are essential for an adequate assessment of the anionic species. The best level of theory predicts that the energy of lowest doublet states of trans form are 1.7 kcal/mol higher than the neutral singlet one. The doublet *cis* form lies at least 8 kcal/mol above the trans form.

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