

A Theoretical Study of Some Bicyclic Azoalkanes

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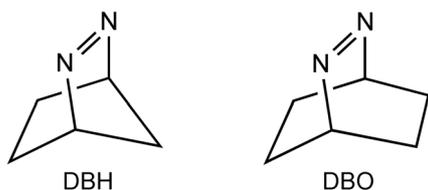
The molecular structures of the ground and lowest triplet states of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH), 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) and their fused ring derivatives are investigated with an *ab initio* method and the density functional theory. Unlike the singlet DBH and DBO, the azo skeletal structures of the triplet counterparts are turned out to be quite sensitive to the change of the electronic structure of the fused ring. The B3LYP C-N=N-C dihedral angles of the triplet DBH and DBO are estimated to be about 28.0 and 40.4°, respectively. The B3LYP singlet-triplet energy gaps for DBH and DBO are predicted to be 58.4 and 48.4 kcal/mol, respectively. The triplet state energy can be lowered drastically by the presence of the remote π - π interaction as in the case of **1bb'**.

Key Words : *Ab Initio*, DFT, DBO, DBH, Singlet-triplet energy gap

Introduction

Some organic compounds with azo (-N=N-) functional group have long been investigated in photochemical and organic experiments.¹⁻⁴ In particular, deazetization (nitrogen loss) of azoalkanes is known to be one of the important routes of formation of photochemically active azo radicals and diradicals.⁵⁻⁸ Extensive studies for verifying the mechanisms of such reactions have been reported.¹⁻¹³ The electronic structure of azo chromophores is also believed to play a key role in determining the reaction mechanism and photochemical properties of many azoalkanes.⁵⁻⁸ The relative energies of their ground and excited electronic states appear to be useful in explaining some reaction mechanisms involving azo species.^{6,14-16} In addition, the processes like intersystem crossing (ISC) between the states of different spin multiplicities may become important in interpretation of their reaction mechanisms.^{2,6,17}

Some bicyclic azoalkanes such as 2,3-diazabicyclo[2.2.1]-hept-2-ene (DBH) and 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) are especially of interest because of their unique photochemical behaviors.^{1,3,5,7} Due to their structural rigidity of such bicyclic azoalkanes, it is relatively easy to detect and characterize their electronic excited states.



Despite the similarities in their structures, the DBO and DBO are known to exhibit quite different photochemical behaviors.^{1,5,13} For example, the quantum yield of the N₂ dissociation of the DBH derivatives is close to unity, while the DBO derivatives show very low decomposition quantum yield. The fluorescence behaviors are also different. Unlike

the DBH systems, many DBO derivatives show strong fluorescence in gas phase.^{1,5,13}

The present study reports the molecular and electronic structures of some derivatives of the DBH and DBO calculated with the density functional theory as well as an *ab initio* method. The structural feature and isomerism of the DBH and DBO systems will be closely examined with Hartree-Fock theory and DFT of Becke's three-parameter-hybrid method using the Lee-Yang-Parr correlation functional (B3LYP).^{18,19} In addition, the singlet-triplet energy gaps of the DBH and DBO systems will be closely examined to figure out the major factors affecting the energy gap.

Computational Details

All calculations were performed using the GAMESS electronic structure program.²⁰ In order to find the correct optimum structures, the restricted and unrestricted Hartree-Fock (RHF and UHF) calculations were carried out with the 6-311G(d) basis set. The molecular geometries for singlet ground state of the DBH and DBO derivatives were fully optimized at the RHF and the B3LYP levels of theory with the 6-311G(d) basis sets. The optimum structures for the first excited triplet states of the DBH and DBO systems were calculated at the UHF and unrestricted B3LYP (UB3LYP) levels of theory. It has been known that the DFT calculation for open shell system is much safer than the MP2 calculation with respect to the spin contamination arising from electronic states with higher multiplicities.²¹⁻²³ According to the result of recent theoretical study,⁸ the UB3LYP and CASPT2 calculations show excellent agreement in predicting the energetics of DBO and DBH systems. Thus, it is clear that the B3LYP (UB3LYP) method with standard 6-311G(d) basis set is good choice to predict the molecular properties for much larger DBH and DBO derivatives with fused rings. The B3LYP vibrational frequency calculations show that all optimized structures are on real local minima without the imaginary frequency.

Results and Discussion

Structural Features.

A. DBH and DBO Derivatives with a Fused Monocyclic Ring: The molecular structures of several DBH and DBO derivatives with a fused monocyclic ring are illustrated in Figure 1. Some important geometrical parameter such as the N=N bond lengths and the C-N=N-C dihedral angles are summarized in Table 1.

The B3LYP N=N bond length of singlet DBH is computed to be 1.245 Å which is somewhat longer for the singlet DBO. According to the previous theoretical study for azomethane, the N=N bond length was reported to be about 1.21 Å.^{6,8} The increase of the N=N bond length in bicyclic azoalkane compared to the simple azoalkane appears to be due to the enhanced p character arising from angle strain in bicyclic species. In the case of triplet state, the N=N bond length in DBO is shorter compared to DBH.

The fact that the singlet N=N bond lengths of DBO and DBH derivatives with a fused monocyclic ring are almost the same reflects the structural rigidity of these species. The size of fused ring and existence of π bond in the ring hardly affect the N=N bond distance of the singlet species. The C-N=N-C dihedral angles of all derivatives are estimated to be 0.0°. In other words, the electronic structure of azo functional group in the singlet DBO and DBH systems is virtually independent of the presence of the neighboring ring. It is

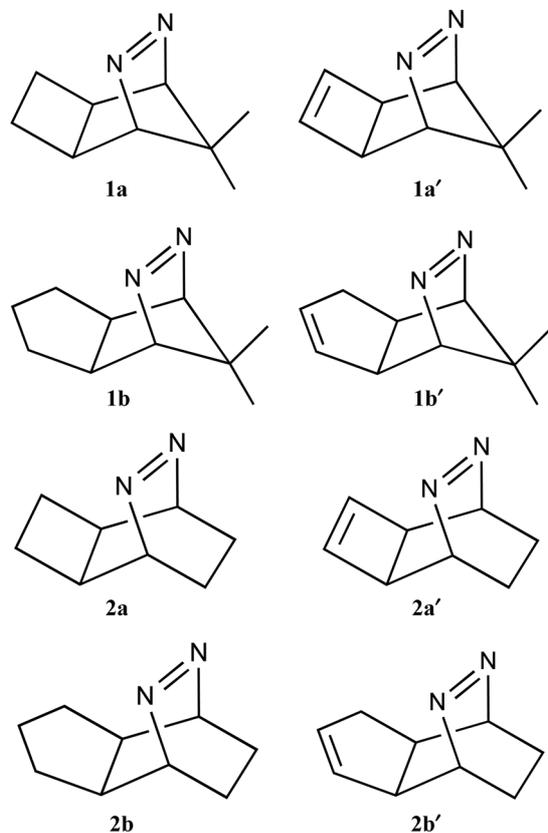


Figure 1. Structures of several DBH and DBO derivatives with a fused monocyclic ring.

Table 1. Computed N=N bond lengths, C-N=N-C dihedral angles and triplet energies for several monocyclic ring fused DBH and DBO derivatives at the B3LYP/6-311G(d) level

	Singlet		Triplet		S-T gap (in kcal/mol)
	N=N bond length	C-N=N-C dihedral angle	N=N bond length	C-N=N-C dihedral angle	
1a	1.248	0.0	1.287	21.7	56.6
1b	1.247	0.0	1.287	20.1	56.8
1a'	1.246	0.0	1.283	18.2	58.3
1b'	1.246	0.0	1.289	21.2	56.9
2a	1.246	0.0	1.284	38.1	47.3
2b	1.246	0.0	1.284	38.6	47.0
2a'	1.244	0.0	1.281	36.1	49.7
2b'	1.245	0.0	1.284	37.7	48.0
DBH	1.245	0.0	1.301	28.0	58.4
DBO	1.263	0.0	1.286	40.4	48.4

also shown from Table 1 that the N=N bond lengths for triplet species are longer than those of singlet species. The B3LYP calculation estimates the value of N=N bond length of all DBH and DBO derivatives to be around 1.28 Å. The triplet N=N bonds become shortened somewhat by the presence of the fused ring. The shortening of the triplet N=N bonds is more pronounced in the DBH systems compared to the DBO systems.

The difference of C-N=N-C dihedral angle between the singlet and triplet states in both DBO and DBH systems are quite dramatic. The previous study at the UHF/6-31G(d) level reported the C-N=N-C dihedral angles of the DBH and DBO to be 30 and 46°, respectively.⁵ The present B3LYP calculation estimates these angles to be 28.0 and 40.4°, respectively. The triplet C-N=N-C dihedral angle decreases in the fused derivatives to some extent. The computed values of C-N=N-C dihedral angle for all DBH derivatives with a fused monocyclic ring are about 18° which is smaller than the DBO angle. In addition, the C-N=N-C dihedral angle of **1a'** with a fused unsaturated four membered ring is somewhat smaller than that of **1b'** with a fused unsaturated five membered ring. Similar decrease of the dihedral angles is also found in the DBO derivatives (**2a'** and **2b'**).

B. DBH and DBO Derivatives with a Fused Bicyclic Ring: The N=N bond lengths and C-N=N-C dihedral angles for some DBH and DBO derivatives with a fused bicyclic ring are summarized in Table 2. Once again, the singlet N=N bond lengths of DBH and DBO derivatives are almost the same as in the cases of the fused monocyclic ring. However, the N=N bond length of **1bb** is significantly longer than the other derivatives. It appears that the N=N bond lengths for the triplet species are quite sensitive to the electronic structure of fused ring, which is somewhat different from the case with a fused monocyclic ring. The triplet N=N bond length of **1bb'** is about 0.1 Å longer than the other triplet cases, which indicates that the electronic environment around the N=N bond in the triplet **1bb'** is somewhat different from the other derivatives.

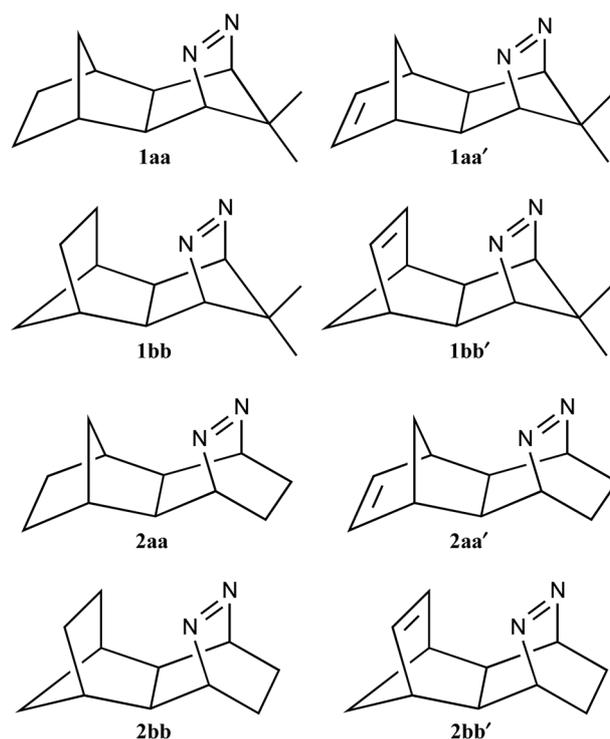
Table 2. Computed N=N bond lengths, C-N=N-C dihedral angles and triplet energies for several bicyclic ring fused DBH and DBO derivatives at the B3LYP/6-311G(d) level

	Singlet		Triplet		S-T gap (in kcal/mol)
	N=N bond length	C-N=N-C dihedral angle	N=N bond length	C-N=N-C dihedral angle	
1aa	1.248	0.0	1.285	17.3	56.8
1aa'	1.247	0.0	1.283	16.8	56.5
1bb	1.268	0.0	1.287	19.9	57.7
1bb'	1.244	0.0	1.391	14.6	39.8
2aa	1.244	0.0	1.274	28.4	49.3
2aa'	1.245	0.0	1.280	32.5	48.8
2bb	1.247	0.0	1.282	36.1	50.2
2bb'	1.246	0.0	1.281	33.9	49.1

The computed C-N=N-C dihedral angles of the triplet DBO and DBH derivatives with a fused bicyclic ring are smaller than the ones with a fused monocyclic ring. It seems that the orientation of double bond in a fused ring affects the C-N=N-C dihedral angle of the triplet species. In DBH derivatives, the C-N=N-C dihedral angles of **1aa** and **1aa'** are almost the same, while the value of **1bb'** is about 2° smaller than that of **1aa'**. It seems that the C-N=N-C skeleton of the triplet DBO system is more flexible than the DBH skeleton. The dihedral angle of **2aa** is about 4 and 6° smaller than that of **2aa'** and **2bb**, respectively. It is of course clear that the double bond in **2aa'** does not directly interact with the N=N bond. On the other hand, the dihedral angle of **2bb'** is about 2° smaller than that of **2bb**. It should be pointed out that there is possibility of π - π interaction between the two remote π bonds in the fused DBH and DBO derivatives. The existence of remote π - π interaction between C=C and N=N in triplet **1bb'** has been confirmed from the previous study.⁵ If the small value of the C-N=N-C dihedral angle is one of the factors fortifying the remote π - π interaction, it can be suggested that the π (C=C)- π (N=N) interaction in triplet **2bb'** is somewhat weaker than **1bb'** since the angles of **1bb'** and **2bb'** differ by about 18°.

Energy of Lowest Triplet State. The energy of difference between the ground and the lowest triplet states of various DBH and DBO derivatives are also summarized in Table 1 and 2. The B3LYP energies of the triplet states of DBH and DBO are computed to be 58.4 and 48.4 kcal/mol higher than their ground states, respectively. According to the previous experimental studies, the gap was reported to be 59-65.5 kcal/mol for DBH and 53-56.5 kcal/mol for DBO. On the other hand, the triplet energies of the DBO and DBH derivatives with a fused monocyclic ring do not appear to be affected by the presence of the fused ring.

In case of the derivatives with a fused bicyclic ring, the triplet energies are about the same as those of the derivatives with a fused monocyclic ring except for **1bb'**. The lowest triplet state of **1bb'** lies 39.8 kcal/mol above the singlet ground state. This value is about 17 kcal/mol lower than its structural isomer of **1aa'**. As discussed briefly above, it is

**Figure 2.** Structures of several DBH and DBO derivatives with a fused bicyclic ring.

likely that the remote π (C=C)- π (N=N) interaction in **1bb'** affects significantly the electronic structure of triplet state. The situation is quite different in the DBO analogue of **2bb'**. The computed singlet-triplet energy gap of 49.1 kcal/mol in **2bb'** is almost the same as that of its structural isomer of **2aa'**. Figure 3a and 3b shows HOMO and LUMO for singlet **1bb'**. The LUMO with the π (N=N)- π (C=C) interaction, as shown in Figure 3b, does not affect the singlet state energy in general. However, this orbital plays an important role in stabilizing the triplet energy of **1bb'** since it is singly occupied in triplet state. However, the effective overlap between two remote π orbitals cannot be observed in the DBO analogue of **2bb'**. (See Figure 3c) This may explain the lack of drastic decrease of triplet energy in **2bb'**.

It is quite natural to expect the remote π - π interaction in some other derivatives with a fused unsaturated monocyclic ring such as **1a'**, **1b'**, **2a'** and **2b'**. There seems to be no such evidence in those cases as far as the stability of the triplet states as shown in Table 1. The orbital analyses in these cases are consistent with the situation found about the N=N bond length and the C-N=N-C dihedral angle.

The stabilization of triplet energy of **1bb'** due to remote π - π interaction can also be confirmed by the comparison of energy difference between the structural isomers. It can be seen in Table 3 that the computed energy differences between some structural isomers in the singlet state are less than about 5 kcal/mol at both RHF and B3LYP levels, which is quite reasonable for such structural isomers. The triplet values are not so much different from the singlet values except for ΔE (**1aa'**-**1bb'**). On the other hand, the energy

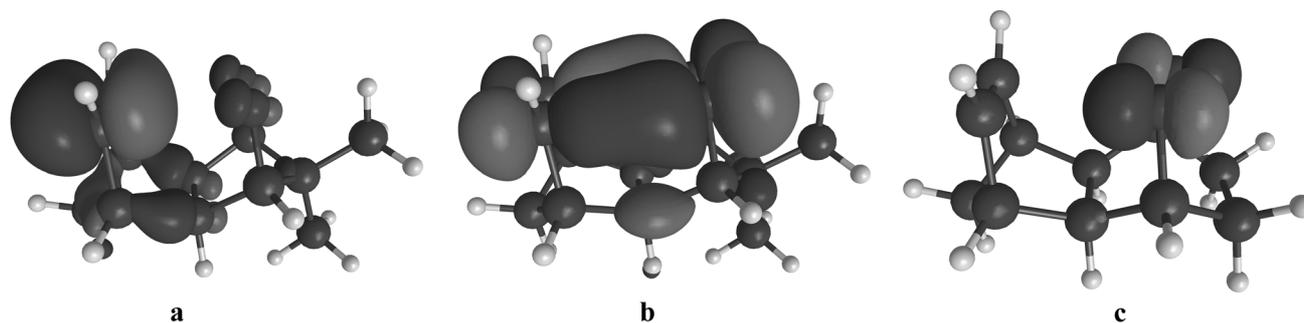


Figure 3. Molecular orbital of (a) HOMO, (b) LUMO for **1bb'** in singlet state and (c) highest SOMO for **2bb'** in triplet state.

Table 3. Computed Energy differences between the two possible isomers of DBH and DBO derivatives with a fused bicyclic ring

	Singlet		Triplet	
	RHF	B3LYP	UHF	UB3LYP
$\Delta E(1aa'-1bb')$	2.8	1.9	-16.5	-14.8
$\Delta E(1aa-1bb)$	3.5	2.4	4.9	3.4
$\Delta E(2aa'-2bb')$	1.8	1.3	2.5	1.8
$\Delta E(2aa-2bb)$	1.5	0.9	2.1	2.0

difference between **1aa'** and **1bb'** in the triplet state is estimated to be about -15 kcal/mol at the UB3LYP level of theory, which is about 13 kcal/mol larger than the energy difference between the saturated isomers without C=C double bond. This result also supports the drastic energy decrease in **1bb'** caused by the remote π - π interaction.

Conclusion

The molecular structures of the ground and lowest triplet states for some bicyclic azoalkanes (DBH and DBO derivatives) are investigated with an *ab initio* method as well as the density functional theory. It is shown that the azo skeletal structures of the triplet DBH and DBO systems are very sensitive to the change of electronic structure of fused ring, whereas their singlet states maintain pretty rigid bicyclic azo skeleton. The C-N=N-C dihedral angles of triplet DBH and DBO are predicted to be about 28.0 and 40.4° at the UB3LYP/6-31G(d) level of theory, respectively. These values somewhat decrease in their fused ring derivatives. The azo functional group of triplet DBO system appears to be more flexible than that of DBH. The triplet C-N=N-C dihedral angles of DBH derivatives are about 18° smaller than those of DBO derivatives. It is also turned out that the triplet C-N=N-C dihedral angles of DBH and DBO derivatives with bicyclic fused ring are somewhat smaller than those of ones with a fused monocyclic ring.

The B3LYP singlet-triplet energy gaps for DBH and DBO are computed to be 58.4 and 48.4 kcal/mol at the B3LYP/6-311(d) level of theory, respectively, which are somewhat smaller than the previous experimental results. The singlet-triplet energy gaps for both DBO and DBH derivatives with a fused ring are not largely different from those of mother

system except for **1bb'** of 39.8 kcal/mol. This drastic energy decrease can be interpreted by the remote π - π interaction between the azo group and the neighboring double bond in the fused ring.

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