Asian Journal of Chemistry Vol. 21, No. 2 (2009), 1210-1216

ab initio Study of Restricted Rotation in N-Nitroso-azirine and N-Nitroso-diaziridine

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Ground state and transition state structures, thermodynamic energies, dipole moments, rotational barrier energies around the N-N bond have been determined using density functional theory based method at the B3LYP/6-31G(d,p) level of theory, using Gaussian 98 package programs. There are two equivalent ground state conformers, A and D in N-nitroso-azirine. The rotational energy barrier of nitroso group is calculated to be 13.14 kJ/mol. There are two equivalent ground state conformers, A and C in N-nitroso-diaziridine. The rotational energy barrier of nitroso group is calculated to be 19.71 and 12.05 kJ/mol. In this work, the inversion energy barrier of nitroso group was also calculated as 23.60, 29.41 and 40.42 kJ/mol for N-nitroso-azirine and N-nitroso-diaziridine, respectively.

Key Words: Restricted rotation, Rotational energy barrier, DFT method, Inversion energy.

INTRODUCTION

Nitrosamines are biologically important compounds as cancer suspect agents[1]. N-nitrosamines are also widely included in many consumer products[2]. In nitrosamine compounds, the N-NO single bond acquires a partial double bond character due to the simultaneous presence of an electron-donating and an electron-accepting group, which coud be explained by the resonance models. Owing to the contribution of the resonant dipolar canonical structure, the rotation around the single bond is somewhat restricted. This effect explains the occurrence of an extra energy of rotation in such molecules[3]. The restricted rotation about the single N-N bond in open chain and cyclic nitrosamine compounds has motivated several experimental and theoretical investigations[3-5]. The NMR technique has been frequently utilized in these experimental investigations. Haky *et al.*[4] studied the isomer populations and rotational barriers in some five-membered cyclic nitrosamine compounds. Fletcher *et al.*[5] used both the dynamic NMR technique and *ab initio* method to evaluate the barrier energy of rotation in nitrosobenzene derivatives. Although the dynamic NMR represents a suitable technique for the determination of the rotational barrier energy and

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particularly the investigation of restricted rotation about the single N-N bond, it cannot usually provide any direct information about the molecular ground or transition states. Although the free energy of activation obtained by the coalescence method is reliable, the resulting data of enthalpy and especially the entropy of activation could be erroneous[3]. The theoretical methods particularly the density functional theory (DFT) provide powerful approaches for the determination of structural geometry, evaluation of molecular ground and transition state energies[6-12].

Since three-membered ring compound has large ring strain, three-membered ring with nitrosamine compounds are structurally interesting compounds. Structural studies of N,N-dimethyl nitrosamine show a planer heavy atom structure[3-7]. This heavy atom planarity has been explained by partial double bond character between the amino and nitroso nitrogen. This partial double bond character also inhibits the nitroso group rotation around the N-N bond and makes high nitroso group rotational energy barrier. The ground state, the nitroso group rotational energy barriers and aziridine ring inversion barriers of N-nitroso-aziridine, N-nitroso-oxaziridine and N-nitroso-dioxaziridine have been investigated[1,2]. Here three-membered ring nitrosamine studies were extended to the N-nitroso-azirine (I) and N-nitroso-diaziridine (II). In this contribution we have studied the rotation around the N-N bond and have suggested that the changes of energy barrier can be correlated to the nature of a bonding interaction.

COMPUTATIONAL DETAILS

Geometry optimization and frequency calculation were performed using the hybrid DFT method at B3LYP/6-31G(d,p) level of theory utilizing Gaussian 98 program package[13-16]. First I and II were fully optimized during the calculation to find the ground state configuration. Since there are two imino nitrogens in the N-nitroso-diaziridin, N_1 and N_2, two different ring inversion transition states can be calculated. For the energy profile of the nitroso group internal rotation, the nitroso group was set to be eclipsed with the N_1-X_3 bond (Fig. 1) in the three-membered ring and then the nitroso group was rotated counterclockwise 10 ° increment. In the nitroso group rotational energy barrier calculation, all geometric parameters were

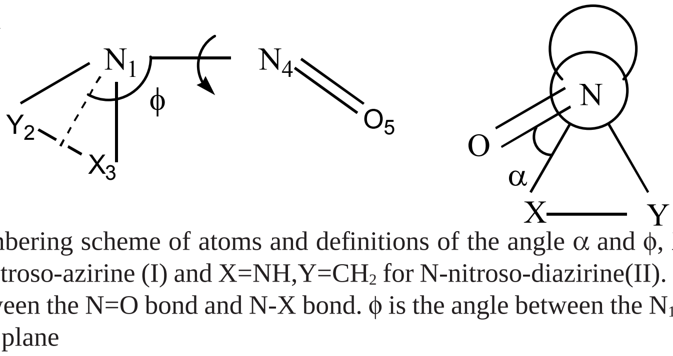

Fig. 1. Numbering scheme of atoms and definitions of the angle α and ϕ, X=Y=CH for N-nitroso-azirine (I) and X=NH,Y=CH_2 for N-nitroso-diazirine(II). α is the angle between the N=O bond and N-X bond. ϕ is the angle between the N_1-N_4 bond and ring plane

allowed to relax except group twisting angle. All transition states were confirmed by one and only one negative eigenvalue in Hessian matrix. At each twisting angle the thermodynamic data have been calculated using the frequency calculations and summary of it have been shown in Table-1.

TABLE-1
THERMOCHEMISTRY DATA (in hartree) USED FOR THE CALCULATION OF THE HEAT OF FORMATION OF CONFORMERS OF THE N-NITROSO-AZIRINE AND N-NITROSO-DIAZIRIDINE FOR ONE STEP

	N-Nitroso-azirine	N-Nitroso-diaziridine
Zero-point correction	0.039669	0.054794
Thermal correction to energy	0.044657	0.059492
Thermal correction to enthalpy	0.045602	0.060436
Thermal correction to Gibbs free energy	0.012036	0.027311
Sum of electronic and zero-point energies	-261.876118	-279.165918
Sum of electronic and thermal energies	-261.871129	-279.161219
Sum of electronic and thermal enthalpies	-261.870185	-279.160275
Sum of electronic and thermal free energies	-261.870185	-279.193400

In this work, *ab initio* calculations were performed at the B3LYP/6-31G(d,p) level of theory to determine the ground state configurations and the corresponding energies and also the hindered rotation around nitrogen atom. The results of frequency calculations have been used to determine the enthalpies of formation of ground states and saddle points.

RESULTS AND DISCUSSION

N-Nitroso-azirine (I): The calculated enthalpies of formation as a function of the rotation angles for N-nitroso-azirine are shown in Fig. 2 and a set of enthalpies of formations for importance state have been presented in Table-2. There are two equivalent ground state conformers, A and D (Fig. 2). The rotational energy barrier of nitroso group is calculated to be 13.14 kJ/mol. The structure of rotational transition state of I shows that the nitroso group is eclipsed with the lone pair of the imino nitrogen in the azirine ring, as shown in the previous studies[17]. For the ground state of I, the nitroso group is twisted 63.82 degree from the N_1-C_2 bond in the azirine ring toward the lone pair of the imino nitrogen. This twisting is general phenomenon in this type of compounds, three-membered ring notrosamines[17].

The angle between the N_1-N_4 bond and the ring plane (ϕ in Fig. 1) is calculated to be 275.63 degree in the ground state, compared to the corresponding angle in 1*H*-azirine[18], 128.5 °. Thus one can conclude that the planarity around imino nitrogen is increased when the azirine ring incorporated with the nitroso group. The structure of the azirine ring inversion transition state shows a planar configuration around the imino nitrogen. The azirine ring inversion energy barrier is calculated to be 23.60 kJ/mol. This high inversion energy barrier can be explained by the antiaromatic effect in the ring inversion of I.

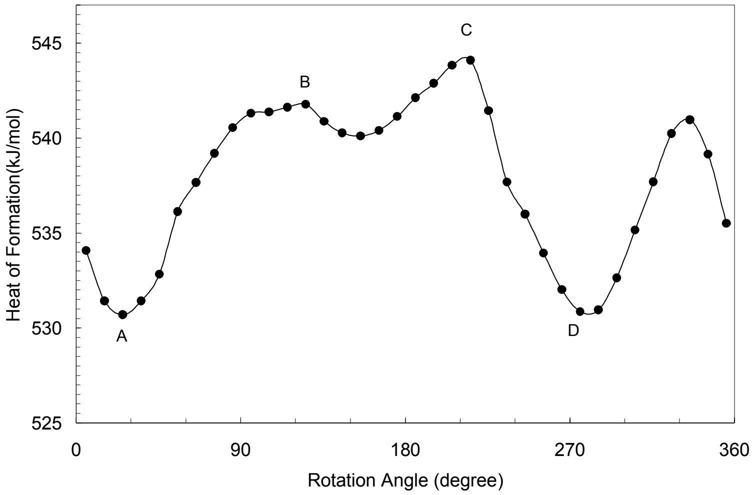

Fig. 2. Heats of formation as a function of rotation of nitroso group for N-nitroso-azirine (I). A and D are nearly equivalent ground state

TABLE-2
CALCULATED HEATS OF FORMATION AND ENERGY BARRIER (kJ/mol)

Compound	Heat of formation			Energy barriers	
	Gs	TS-Rot	TS-Inv	Rot	Inv
N-Nitroso-azirine	530.95	544.09	554.54	13.14	23.60
	365.64	377.69	395.05	12.05	29.41
N-nitroso-diaziridine	364.30	384.00	404.72	19.71	40.42

Since the structure of the ring inversion transition state of I has four π electrons and that of the ground state has two π electrons, the former shows antiaromaticity and the latter shows aromaticity. The ground state of I is more stable than that of N-nitroso-aziridine and the azirine ring inversion transition state of I is less stable than that of N-nitroso-aziridine. Consequently the three-membered ring inversion energy barrier of I is larger than that of N-nitroso-aziridine.

N-Nitroso-diazirindine (II): Since the hydrogen atom at N_3 (Fig. 1) in the diaziridine ring is nonsymmetric, there are two possible conformer for N-nitroso-diaziridine (II). The hydrogen attached N_3 in the diaziridine ring can have *anti* and *syn* conformations with respect to the nitroso group. The heat of formation of conformers which produced from the rotation of nitroso group around the N_1-N_4 bond have been presented in Fig. 3. A subset of heats of formation for selected structures present in the Table-2. One can see that the nitroso group rotational energy profile of II has two energy minima, which are the ground states A and C. The ground state structure of II shows that the nitroso group is placed between the lone pair of the imino nitrogen N_1 and the N_1-N_3 bond in the diaziridine ring.

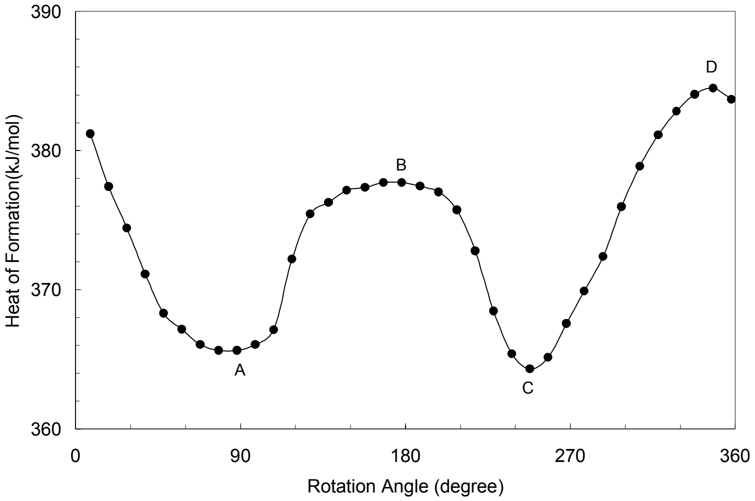

Fig. 3. Heats of formation as a function of rotation of nitroso group for N-nitroso-diaziridine. A and C are nearly equivalent ground state

The nitroso group preferred the more electronegative side, the N_1-N_3 bond, than the less electronegative side, the N_1-C_2 bond, in the diaziridine ring, which is called the anomeric effect. The heats of formations are 365.64 and 364.30 kJ/mol for the ground states A and D in II, respectively. The structure of the nitroso group rotational state in II shows that the nitroso group is nearly eclipsed with the lone pair of the imino nitrogen N_1. The heat of formation of the nitroso group rotational transition state in II is 377.69 kJ/mol. Thus the rotational energy barriers of the nitroso group in II are calculated to be 12.05 kJ/mol from the maxima B to the ground state and 13.39 kJ/mol from the ground state to the D configuration.

Since N-nitroso-diaziridine has two imino nitrogens in the diaziridine ring, there are two nitrogen, inversion sites *i.e.*, N_1 and N_3 (Fig. 1). The structure of the inversion transition state shows that the imino nitrogen, N_1 or N_3, has planar configuration. The heat of formations of the inversion transition states are 395.05 and 404.72 kJ/mol for the N_1 and N_3 sites, respectively. The structure of the N_1 inversion transition state shows that the nitroso group is nearly eclipsed with the diaziridine ring. However, the structure of the N_3 inversion transition state shows that the nitroso group is twisted 86 º which is similar to the ground state structure. The N_1 imino nitrogen inversion energy barriers in II are 29.41 kJ/mol. The N_3 imino nitrogen inversion energy barriers in II are 40.42 kJ/mol. The calculated heat of formations, energy barriers and selected geometric parameters have been shown in Table-3.

There are three major effects considered here, (i) the conjugation between the lone pair of the imino nitrogen N_1 and the nitroso group double bond, (ii) the dipole-dipole repulsion between the lone pair of the imino nitrogen N_1 and the lone pair of the nitroso nitrogen N_4 and (iii) the strict hindrance between the nitroso group

TABLE-3
STRUCTURAL PARAMETERS OF N-NITROSO-AZIRINE (I)
AND N-NITROSO-DIAZIRIDINE (II)

	I			II					
	GS	TS-Rot	TS-Inv	GS(1)	TS-Rot(1)	GS(2)	TS-Rot(2)	TS-Inv(1)	TS-inv(2)
Bond	(Distances (Å))								
N_1-C_2	1.461	1.477	1.439	1.434	1.545	1.442	1.529	1.436	1.519
N_1-C_3	1.471	1.493	1.510	1.434	1.464	1.443	1.454	1.383	1.368
N_1-N_3	1.516	1.497	1.285	1.464	1.505	1.466	1.509	1.325	1.385
N_1-N_4	1.077	1.075	1.075	1.088	1.088	1.087	1.182	1.161	1.167
N_4=O_5	1.073	1.076	1.079	1.023	1.022	1.022	1.438	1.521	1.238
	Angles (º)								
$C_2N_1C_3$	115.4	110.6	113.4	116.7	112.2	117.1	106.7	122.5	125.6
$C_2N_1N_3$	112.5	113.5	62.7	115.2	107.0	109.9	100.9	127.6	121.7
$N_1N_4O_5$	137.1	138.7	112.0	118.3	117.6	117.8	109.9	131.2	122.9
ϕ*	275.7	215.6	179.9	247.2	337.9	78.1	178.1	179.9	126.3
α*	56.1	55.1	0.0	68.49	61.4	65.8	63.6	3.6	45.7

*ϕ and α are defined in Fig. 1.

and three-membered ring. In the planer configuration around N_1, which is the inversion transition state of I and II, the maximum hyperconjugation can be possible between the lone pair of the imino nitrogen N_1 and the nitroso group double bond. Thus the inversion transition states of I and II are stabilized by this interaction. Also in the ground state structure of I and II, the nitroso group makes nearly 90 º with the lone pair of the imino nitrogen N_1. And then the nitroso group double bond makes nearly parallel with the lone pair of the imino nitrogen N_1, which shows maximum conjugation. When the nitroso group is placed in the middle of the three-membered ring, the dipole-dipole repulsion is very large and the corres-ponding structures have the highest energies. For the highest energy states the strict hindrance is moderate. The rotational transition states of I and II show that the nitroso group is nearly eclipsed with the lone pair of the imino nitrogen N_1. At the nitroso group rotational transition state, the dipole-dipole repulsion is not severe and steric hindrance is also moderate.

Conclusion

The ground state configuration and energies of the N-nitroso-azirine (I) and -diazirine (II) have studied at the density functional theory level using a moderate sized basis set. The ground states geometries of N-nitroso-azirine (I) and -diazirine (II) show that the imino nitrogen N_1 has non-planar configuration. Also in the ground states of I and II the nitroso group is not eclipsed with the three-membered ring. The nitroso group rotational transition states of I and II show that the nitroso group is nearly eclipsed with the lone pair of the imino nitrogen N_1.

ACKNOWLEDGEMENT

Support of this work by the University of Mazandaran Research Council is gratefully acknowledged.

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(*Received*: 11 January 2008; *Accepted*: 25 September 2008) AJC-6894