mass(m/e); 164(M$^+$), 91(M$^+$ + 73), 29(M$^+$-135).

n-propyl phenylacetate: Colorless liquid. ^{1}H-NMR (CCl$_4$); δ 0.78(t, CH$_3$), 1.50(h, CH$_2$), 3.50(s, CH$_2$), 3.93(t, CH$_2$), 7.16(m, Ph). ^{13}C-NMR(CDCl$_3$); δ 10(CH$_3$), 22(2CH$_2$), 42(CH$_2$), 62(CH$_2$), 127(CH), 129(2CH), 134(C), 172(COO). IR(neat); 1726cm^{-1}($\nu_{C=O}$). mass(m/e); 178(M$^+$), 91(M$^+$-87).

Iso-propyl phenylacetate: Colorless liquid. ^{1}H-NMR(CCl$_4$); δ 1.22(d, 2CH$_3$), 3.50(s, CH$_2$), 5.00(h, CH), 7.33(m, Ph). mass(m/e); 178(M$^+$), 91(M$^+$-87).

n-butyl phenylacetate: Colorless liquid. ^{1}H-NMR (CCl$_4$); δ 0.90(t, CH$_3$), 1.34(h, CH$_2$), 1.60(q, CH$_2$), 3.60(s, CH$_2$), 4.10(t, CH$_2$), 7.30(m, Ph). ^{13}C-NMR(CDCl$_3$); δ10(CH$_3$), 19(CH$_2$), 31(CH$_2$), 42(CH$_2$), 65(CH$_2$), 127(CH), 129(2CH), 129(2CH), 134(C), 172(COO). IR(neat); 1726 cm^{-1}($\nu_{C=O}$). mass (m/e); 192(M$^+$), 91(M$^+$-101).

Ethyl-o-chlorophenylacetate: Colorless liquid. ^{1}H-NMR(CCl$_4$); δ 1.26(t, CH$_3$), 3.65(s, CH$_2$), 4.11(q, CH$_2$), 7.20(m, Ph). mass(m/e); 200(M$^+$ + 2), 198(M$^+$), 127(M$^+$-71), 125(M$^+$-73).

Ethyl-p-chlorophenylacetate: Colorless liquid. ^{1}H-NMR(CCl$_4$; δ1.23(t, CH$_3$), 3.50(s, CH$_2$), 4.13(q, CH$_2$), 7.33(q, Ph). mass(m/e); 200(M$^+$ + 2), 198(M$^+$), 127(M$^+$71), 125(M$^+$-73).

Ethyl-o-Tolyacetate: Colorless liquid. ^{1}H-NMR (CCl$_4$); δ1.23(t, CH$_3$), 2.33(s, CH$_3$), 3.52(s, CH$_2$), 4.41(q, CH$_2$), 7.18(m, Ph). mass(m/e); 178(M$^+$), 105(M$^+$-73).

Ethyl-p-tolylacetate: Colorless liquid. ^{1}H-NMR(CCl$_4$) δ1.20(t, CH$_3$), 2.33(s, CH$_3$), 3.48(s, CH$_2$), 4.13(q, CH$_2$), 7.13(q, Ph). mass(m/e); 178(M$^+$), 105(M$^+$-73).

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Semiempirical MO Calculation of Hetero Atom Three-Membered Ring Compounds (I): N-Nitroso-aziridine, -oxaziridine, and -dioxaziridine

Ki Woon Hwang

Agency for Defense Development, Taejeon P.O. Box 35, Taejeon 300-600. Received May 24, 1990

Fully optimized MNDO molecular orbital calculations are described for N-nitroso-aziridine (I), -oxaziridine (II), and -dioxaziridine (III). The ground state geometries show the nonplanar configuration around the imino nitrogen. The nitroso group rotational energy barriers are 3.25, 0.43 and 1.18 kcal/mol for I, II and III, respectively. Also the calculated aziridine ring inversion barriers are 3.98, 15.61 and 27.46 kcal/mol for I, II and III, respectively.

Introduction

N-Nitrosamines are an important class of compounds as environmental carcinogens and they are widely present in many consumer products.[1] Although they have been studied

for several decades in their biochemical behaviors, like carcinogenic properties, their structural infomrations are little known. Experimental[2-5] and theoretical[6] studies of N,N-dimethyl nitrosamine show a planar heavy atom structure. The heavy atom planarity can be explained by partial double bond
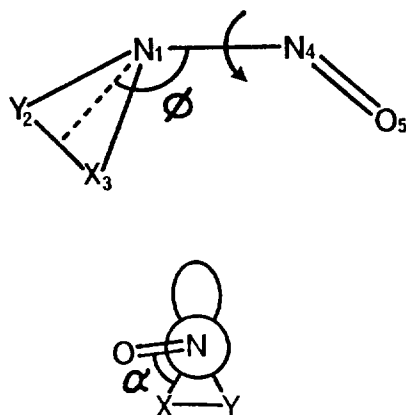
Figure 1. Numbering scheme of atoms and definitions of the angle α and ϕ: a) X = Y = CH$_2$: N-Nitroso-aziridine (I). b) X = O, Y = CH$_2$: N-Nitroso-oxaziridine (II). c) X = Y = O: N-Nitroso-dioxaziridine (III).

character between the amino nitrogen and the nitroso nitrogen. This partial double bond makes hindered rotation of the nitroso group around the N-N bond.

Looney *et al.*[7] have studid hindered rotation in nitrosamines by NMR and reported that N,N-dimethyl nitrosamine has a 23 kcal/mol potential barrier to internal rotation of the nitroso group in neat solution. Gas phase NMR study of N,N-dimethyl nitrosamine[8] reported that the nitroso group internal rotation barrier is 20.5 kcal/mol. MNDO calculation[6] of N,N-dimethyl nitrosamine reported that the nitroso group internal rotation and inversion barriers are 13 and 80 kcal/mol, respectively.

In the aziridine, nitrogen inversion barrier of experimental[9] and theoretical[10] studies have been reported 19.1 and 14.9 kcal/mol, respectively. NMR study of N-methyl aziridine[11] showed that the ring inversion barrier is 19 kcal/mol. Theoretical[10] study of oxaziridine and dioxaziridine showed that inversion barriers are 31 and 50 kcal/mol, respectively.

In the three-membered ring nitrosamines, the atomic orbital of the imino nitrogen in the ring probably has some sp^3 character, because of the three-membered ring strain. The angle CNC in the aziridine ring should be near 60°, not tetrahedral. This small angle prohibits a planar heavy atom structure in the N-nitroso-aziridine and probably makes a lower nitroso group internal rotation barrier. Kirste and Rademacher[12] calculated N-Nitroso-aziridine by MNDO MO method and reported that the nitroso group internal rotation and aziridine ring inversion barriers are 3.38 and 3.66 kcal/mol, respectively. Here revised optimized ground state geometry of the N-Nitroso-aziridine (I) with N-nitroso-oxaziridine (II) and -dioxaziridine (III) are reported. The aziridine ring inversion and nitroso group internal rotation barriers of I, II, and III are also reported.

Calculation Method

MNDO[13] MO method in the AMPAC[14] program package was used throughout. The AMPAC program was modified for the CDC CYBER 180/860 and run at NOS/VE. All calculations were performed by using standard RHF SCF procedures. I, II, III were fully optimized to find ground state con-

TS-1   **TS-2**

GS-1   **GS-2**
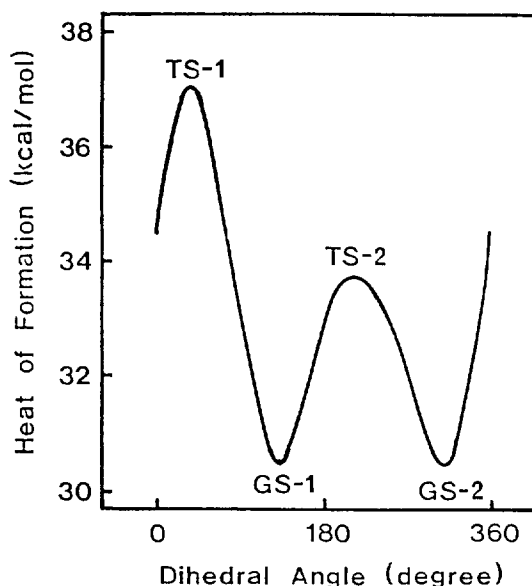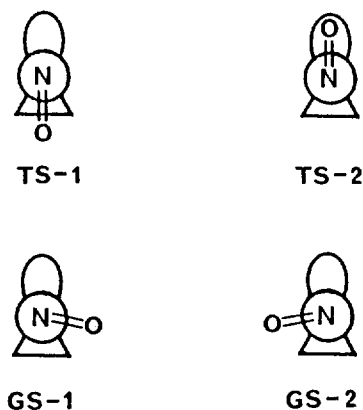
Figure 2. The nitroso group internal rotational energy profile of the N-nitroso-aziridine (I). TS-1: The global maximum. TS-2: The rotational transition state (TS-Rot). GS-1 and GS-2: The equivalent ground state (GS).

formations. For a transition state of an aziridine ring inversion barrier, the imino nitrogen in the ring was set to the planar configuration. For the energy profile of the nitroso group internal rotation, the nitroso group was set to be eclipsed with the X$_3$-N$_1$ bond (see Figure 1.) in the aziridine ring and then nitroso group was rotated counterclockwise 10° increment. In the rotational barrier calculations, all geometric parameters were allowed to optimize except the nitroso group twisting angle. To find the rotational transition states, the nitroso group twisting angle was rotated 1° increment around the energy maximum and finally rotated 0.1° increment. All transition states were confirmed by one and only one negative eigen value in the Hessian matrix.

Result and Discussion

N-Nitroso-aziridine (I). This study most agrees previous reported geometric parameters and heat of formations[11] except dihedral angle α. Figure 2. shows nitroso group rotational energy profile of I. There are two equivalent ground state conformers, GS-1 and GS-2. The rotational en-

Table 1. Calculated Heat of Formations and Energy Barriers

Compounds	Heat of formations (kcal/mol)			Energy barriers	
	GS	TS–Rot	TS–Inv	Rot.	Inv.
N-nitroso					
–aziridine (I)	30.49	33.74	34.47	3.25[a]	3.98[b]
N-Nitroso	24.31[c]	27.03	39.92	2.72[d]	15.61
–oxaziridine (II)	26.60[e]			0.13[f]	
N-Nitroso					
–dioxaziridine (III)	66.91	68.09	94.37	1.18	27.46

[a] 3.38 kcal/mol in Ref. 12. [b] 3.66 kcal/mol in Ref. 12. [c] Heat of formation of the ground state. [d] Energy barrier from the ground state to the local minimum. [e] Heat of formation of the local minimum. [f] Energy barrier from the local minimum to the ground state.

ergy barrier is 3.25 kcal/mol. The structure of the rotational transition state shows that the nitroso group is eclipsed with the lone pair of the imino nitrogen. In the ground state of I, the nitroso group is twisted 52.9° from the C–N bond in the aziridine ring toward the lone pair of the imino nitrogen. Usually double bonds, such as C = O or N = O in esters, ketones, nitrates and nitrites, are eclipsed with the single bonds of alkyl group. This nitroso group twisting in I is probably characteristic property of the three-membered ring. Two major effects can be considered here. One is the steric hindrance between the nitroso group and the aziridine ring. Since three–membered ring compound is highly strained, the bond orbital in the ring can be expailned by bent bond orbital toward outside of the ring. The repulsion of the nitroso group with the bent bond is probably

severe. Another is the conjugation between lone pair of the imino nitrogen and the nitroso group. The maximum conjugation can be possible between the lone pair of the imino nitrogen and the nitroso group double bond when the dihedral angle between the lone pair of the imino nitrogen and the nitroso group is nearly perpendicular. Thus the nitroso group is twisted from the C–N bond in the aziridine ring. The structure of the aziridine ring inversion transition state is planar configuration around the imino nitrogen. The aziridine ring inversion barrier in I is 3.98 kcal/mol. The ring inversion barrier of I is smaller than those of aziridine[9], and N-methyl-aziridine[11], 19.1 and 19.0 kcal/mol, respectively. The calculated heat of formations and energy barriers are shown in Table 1.

The ground state bond distance N_1–N_4, 1.359 Å, is smaller than that of the rotational transition state, 1.397 A, and larger than that of the ring inversion transition state, 1.320 Å. The ground state bond distance $N_4 = O_5$, 1.166 Å, is larger than that of the rotation transition state, 1.160 Å, and smaller than that of the ring inversion transition state, 1.169 Å. The two bond distances trends are well matched with bond orders trends of the N_1–N_4 and $N_4 = O_5$. The bond orders between N_1 and N_4 are 1.01, 0.93, and 1.07 for GS (the ground state), TS–Rot (the rotational transition state), and TS–Inv (the inversion transition state), respectively. Since the lone pair of the imino nitrogen is eclipsed with the nitroso group in TS–Rot, there is no overlapping between the nitroso group double bond and the lone pair of the imino nitrogen. Thus TS–Rot has the smallest bond orders between N_1 and N_4 compared to GS and TS–Inv. The bond orders between N_4 and O_5 are 1.91, 2.00 and 1.82 for GS,

Table 2. Geometric Parameters, Atomic Charges and Bond Orders of N–Nitroso–aziridine (I), –oxaziridine(II) and –dioxaziridine (III)[a]

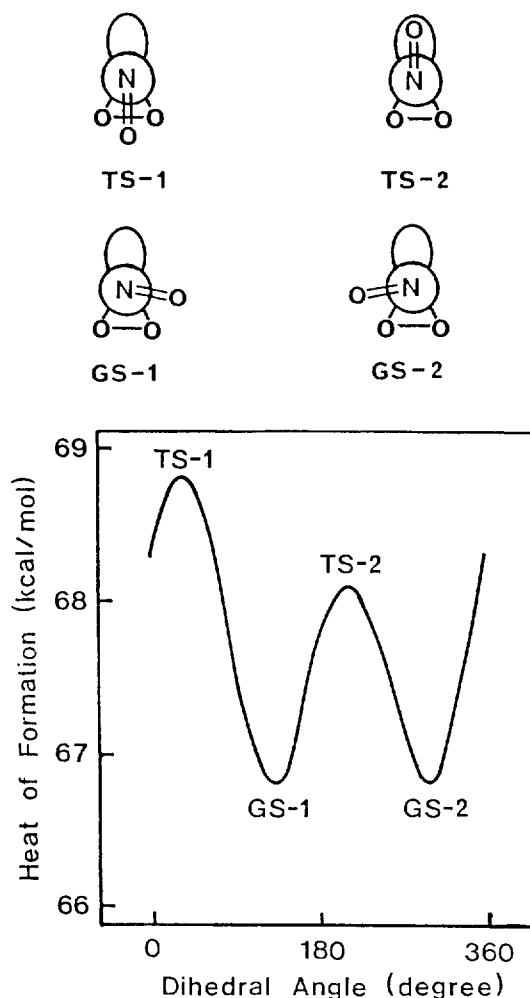|	I			II			III		
	GS	TS–Rot	TS–Inv	GS	TS–Rot	TS–Inv	GS	TS–Rot	TS–Inv
Distances[b]									
N_1–C_2	1.474	1.494	1.448	1.485	1.491	1.439			
N_1–O_2							1.337	1.345	1.318
N_1–C_3	1.483	1.494	1.456						
N_1–O_3				1.350	1.349	1.338	1.348	1.345	1.331
N_1–N_4	1.359	1.397	1.320	1.393	1.429	1.324	1.434	1.458	1.349
$N_4 = O_5$	1.166	1.160	1.169	1.159	1.156	1.162	1.153	1.151	1.154
Angles[c]									
$C_2N_1C_3$	62.0	60.6	64.2						
$C_2N_1O_3$				59.0	59.2	62.4			
$O_2N_1O_3$							59.0	58.8	61.0
$N_1N_4O_5$	116.6	113.3	116.6	118.1	112.8	119.1	116.0	111.8	117.1
ϕ	136.2	122.3	180.0	126.5	118.2	180.0	122.1	115.6	180.0
α	52.9	d	0.0	42.8	d	0.0	51.6	d	0.0
Atom charges[e]									
N_1	–0.349	–0.344	–0.458	–0.171	–0.181	–0.350	–0.005	–0.024	–0.223
N_4	0.240	0.180	0.325	0.195	0.161	0.349	0.195	0.171	0.393
O_5	–0.203	–0.120	–0.270	–0.132	–0.085	–0.231	–0.086	–0.058	–0.183
Bond orders									
N_1–N_4	1.01	0.93	1.07	0.96	0.90	1.04	0.89	0.87	0.96
$N_4 = O_5$	1.91	2.00	1.82	1.98	2.04	1.85	2.04	2.07	1.92

[a] See Figure 1. for the numbering of the atoms. [b] Distance in Å. [c] Angle in degrees. [d] The N = O is syn eclipsed with the lone pair of the imino nitrogen. [e] Electronic unit.

MO Calculation Ring Compd.

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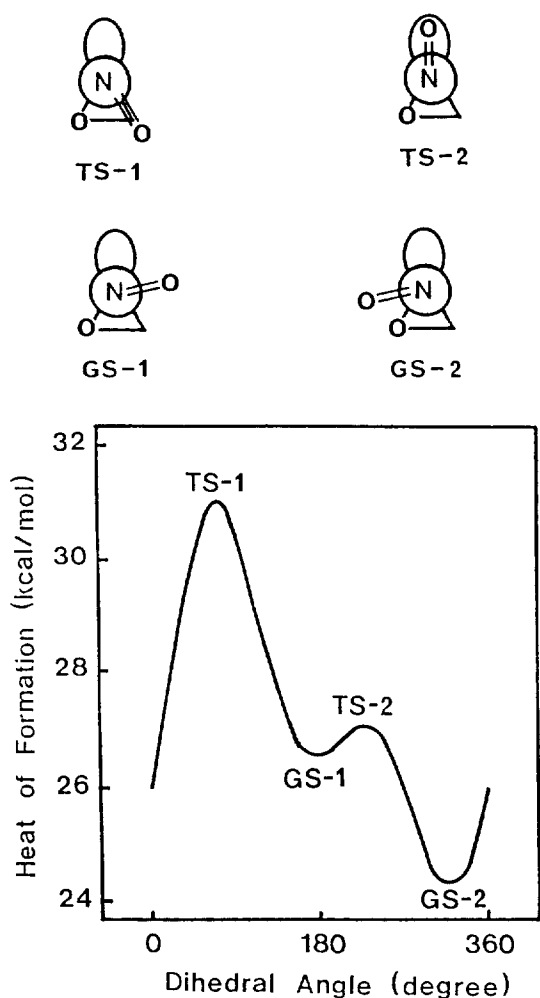
Figure 3. The nitroso group internal rotational energy profile of the N-nitroso-oxaziridine (II). TS-1: The global maximum. TS-2: The rotational transition state (TS-Rot). GS-1: The local minimum. GS-2: The ground state (GS).

Figure 4. The nitroso group internal rotational energy profile of the N-nitroso-dioxaziridine (III). TS-1: The global maximum. TS-2: The rotational transition state (TS-Rot). GS-1 and GS-2: The eqivalent groundstate (GS).

TS-Rot and TS-Inv, respectively. Conjugation between N_1-N_4 and $N_4=O_5$ is the largest in TS-Inv and the smallest in TS-Rot. The order of conjugstion is TS-Inv>GS> TS-Rot. The angles ϕ (see Figure 1.) are 136.2, 122.3 and 180.0° for GS, TS-Rot, and TS-Inv, respectively. These pyramidal angles are compared to the aziridine pyramidal angle,[15] 112.5°. Since the nitroso group is heavier than hydrogen atom, these large angle of I are expected. Also these angles ϕ are well matched with bond orders and conjugation order. Geometric parameters, atomic charges and bond orders of I are summarized in Table 2.

N-Nitroso-oxaziridine(II). Figure 3, shows the nitroso group internal rotational energy profile of II. Since oxaziridine ring is not symmetric, there are two nonequivalent stable conformers. One is the ground state and another is the local minimum. The ground state shows that the direction of the nitroso group is placed between the lone pair of the imino nitrogen and the O-N bond in the ring. That of the local minimum is placed between the lone pair of the imino nitrogen and the C-N bond in the ring. The direction of the nitroso group can be explained by the anomeric effect. The nitroso group prefers more negative side, O-N bond,

than less negative side, C-N bond. In the ground state, the nitroso group is twisted 42.8° from the O-N bond in the aziridine ring toward the lone pair of the imino nitrogen. The nitroso group twisting in the local minimun is 106.9° from the C-N bond toward the lone pair of the imino nitrogen. The heat of formations are 24.31 and 26.60 kcal/mol for the ground state and the local minimum, respectively. The structure of the rotational transition state shows that the nitroso group is eclipsed with the lone pair of the imino nitrogen and heat of formation of the rotational transition state is 27.03 kcal/mol. The rotational energy barriers are 0.43 kcal/mol from the local minimum to the ground state and 2.72 kcal/mol from the ground state to the local minimum of II. The structure of the global maximum shows that the nitroso group is eclipsed with the C-N bond in the ring (see Figure 3). This global maximum structure is different from that of I, the direction of the nitroso group is placed between the C-N bonds in the ring. Probably the repulsion of $N=O$ with C-N is larger than that of N=O with O-N. The structure of the aziridine ring inversion state is same as that of I, the imino nitrogen has planar configuration. The aziridine ring inversion barrier in II is 15.61 kcal/mol. This inversion barrier is

compared to the oxaziridine ring inversion barrier,[10] 32 kcal/mol. The calculated heat of formations and energy barriers are shwon in Table 1. The trend of bond distances and bond orders of II are same as those of I. The dihedral angle ϕ, 126.5°, of the GS is compared to that of oxaziridine, 109.5° Summarized geometric parameters, atomic charges and bond order of II are shown in Table 2.

N-Nitroso–dioxaziridine (III). Figure 4, shows the nitroso group internal rotational energy profile of III. There are two equivalent ground state conformers. The rotational energy barrier is 1.18 kcal/mol. The structure of the ground state shows that the nitroso group is twisted 51.6° from the O–N bond toward the lone pair of the imino nitrogen. The structure of the rotational transition state is that the nitroso group is eclipsed with the lone pair of the imio nitrogen. The structure of the global maximum is same as that of I, the direction of nitroso group is placed between the C–N bonds. The aziridine ring inversion barrier is 27.46 kcal/mol. This inversion barrier is compared to that of dioxaziridine,[10] 50 kcal/mol. The calculated heat of formations and energy barriers of III are shown in Table 1. The treand of bond distances and bond orders of III are same as those of I and II. The dihedral angle ϕ, 122.1°, of ground state is cmpared to that of dioxaziridine, 107.3°. Geometric parameters, atomic charges and bond orders of III are also summarized in Table 2.

The bond distances N_1–N_4 are 1.359, 1.393 and 1.434 Å for the ground state of I, II and III, respectively, and that of N_4 = O_5 are 1.166, 1.159 and 1.153 Å for the ground state of I, II and III, respectively. These increasing trend of bond distance, N_1–N_4 and decreasing trend of bond distance, N_4 = O_5 clearly show that the more oxygen atom presents in the aziridine ring, the more single bond character shows between N_1 and N_4, and the more double bond character shows between N_4 and O_5. The number of oxygen atom is directly related to the conjugation between N_1–N_4 and N_4 = O_5 and the conjugation order is I>II>III. Also the number of oxygen atom affects the energy barriers. As shown in Table 2, the atomic charge density of the imino nitrogen (N_1) decreases as increase of oxygen atom number in the aziridine ring, because of the electronegativity of the oxygen atom. Thus the conjugation between the imino nitrogen and the nitroso group decreases as the number of oxygen atom increases. Consequently as number of oxygen atom increases, the nitroso group rotational energy barrier decreases and the aziridine ring inversion barrier increases (see Table 1).

Conclusion

The ground state geometries of I, II and III show that the imino nitrogen in the aziridine ring has nonplanar configuration. The direction of the nitroso group in the ground state is twisted from the X_3–N_1 bond (see Figure 1.) toward the lone pair of the imino nitrogen. These phenomena are probably characteristic property of three-membered ring nitrosamines. As increase of oxygen atom number in the aziridine ring, the nitroso group internal rotational energy barrier decreases and the aziridine ring inversion barrier increases.

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