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Structural and Kinetic Investigations on Nitrogen Inversion of Some Aziridine Compounds Using Density Functional Theory Study

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Using density function theory methods (B3LYP) the molecular structures of various substituted aziridine compounds, both in their ground states as well as their planar shaped transition states, corresponding to nitrogen inversion process, were determined. The energy, enthalpy, free energy changes along with the activation energy and rate constants for such nitrogen inversions were determined for these substituted aziridine compounds. The impacts of introduction of substituents like methyl, ethyl, isopropyl, phenyl on nitrogen inversion were determined. The change of barrier energy for nitrogen inversion on changing the substituent on N-atom of the aziridine ring was also determined. The results predict that introduction of electronegative element on N-atom of the aziridine moiety leads to an increase in energy barrier; the out of ring substituent also increases the barrier energy towards such inversion. Thus such increase in barrier energy will facilitate the isolation of various chiral aziridine units.

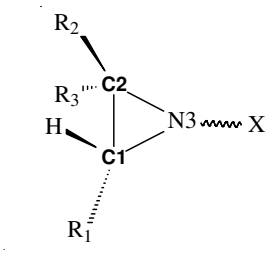
Key Words: Nitrogen inversion, DFT, Transition state theory, IRC, Optical activity, Kinetic parameters.

INTRODUCTION

Nitrogen compounds of the type $NR_1R_2R_3$ in which nitrogen carries three different groups is not superimposable on its mirror image and thus should exist as enantiomeric pair. But it is impossible to isolate these enantiomers as the activation energy between the two enantiomers is too small resulting in very rapid interconversion between them due to nitrogen inversion. At room temperature, this energy barrier is 6-7 kcal/mol[1,2]. The rapid interconversion is somewhat restricted when nitrogen forms a three membered heterocycle *i.e.*, aziridine. This is due to the increase in activation energy compared to acyclic amines. The impact of angle strain and electronic effect on N-inversion of aziridine is a subject of many experimental research works[2-6].

The density functional theory (DFT) is currently being applied for carrying out a variety of quantum chemical calculations ranging from geometry optimization of large clusters to the study of reaction rates[7,8]. For theoretical prediction of spectroscopic properties (transition energy, oscillator strength *etc*.), the time dependent density functional theory (TDDFT) has been developed[7,9] and is now being widely used[10]. The application of such theoretical studies on predicting various properties of different aziridine compounds due to N-inversion has just began[11] and lots of works are still to be done to gain a better knowledge on such an important three membered heterocycle.

In this work, the impact of various out of the ring substituent on N-inversion in aziridine ring using density function theory (B3LYP) method is reported. The rates of racemization, activation energy, $\Delta G^{\#}$ of the compounds under investigation are also calculated. Fig. 1 gives a view of a general aziridine moiety with various substituents considered for our theoretical investigation.



X = Cl, Br
R_1 = CH_3, CH_3CH_2, $(CH_3)_2CH$, C_6H_5
R_2 = H, CH_3 ; R_3 = H, CH_3

Fig. 1. View of a general aziridine moiety

COMPUTATIONAL METHOD

All computations were performed on a Pentium computer with Gaussian 03 Revision D.01 suite of programmes[12]. DFT

calculations were done by using the Becke's three parameter hybrid[13] exchange potential with the correlation function of Lee, Yang and Parr[14] (B3LYP). The basis set used were uniformly 6-31++G(d,p). The geometries of the reactants, products, transition states (TS) were optimized and the harmonic vibrational frequencies, zero point energies (ZPE) and thermochemical quantities were calculated for finding the minimum energy path (MPE) by the intrinsic reaction coordinate (IRC) theory[15] at the DFT/B3LYP/6-31++G(d,p) level. The calculated transition states were confirmed to have one imaginary frequency. All the energies quoted and discussed in the present paper include the ZPE correction. The rate constant for racemization have been calculated using the conventional transition state theory[16,17]:

$$k(T) = \chi(T)\frac{k_B T}{h}.e^{-\frac{\Delta G^{\#}}{RT}} = Ae^{-\frac{E_a}{RT}}$$

where k_B is the Boltzmann constant, h is the Plank constant, $\Delta G^{\#}$ is the change in Gibbs free energy (between initial reactant structure and transition state structure), R is the ideal gas constant, A is the pre-exponential factor E_a represents the activation energy and $\chi(T)$ accounts for the tunneling effects.

RESULTS AND DISCUSSION

Geometrical structure: Using density function theory method (B3LYP) the structural geometrical parameters of the aziridine compounds, both in the equilibrium state and the planar shaped transition state (TS) structures were determined. Fig. 2 shows a typical sequence of nitrogen inversion of a general aziridine molecule with atom labels. The results are reported in Table-1.

For all the halogen derivatives (Cl/Br) under investigation, the C1-C2 bond length increases on planarization (TS) by about 0.1 Å whereas, both C1-N and C2-N bond lengths are compressed by about the same amount. The N-X (X = Cl/Br) bond length for all the compounds are compressed (by 0.08-0.1 Å) in the TS form. The bond angles C2C1C8, for all the compounds shortens but C1NX and C2NX (X = Cl/Br) bond angles increases on going from the equilibrium state to the TS structure. The change of dihedral angle away from the N-X bonds are insignificant, suggesting that N-inversion in the above compounds has very little impact on the other atoms, both in the ring and substitution, away from this bond.

Kinetic aspects of N-inversion: $\Delta E^{\#}$, $\Delta H^{\#}$, $\Delta G^{\#}$ energy barrier values for N-inversion are calculated. The calculated values are given in Table-2. $\Delta E^{\#}$ is the difference between the corrected $E^{\#}$ values of the planar shaped transition state and the initial quasi-pyramidal structure in its lowest energy state. The table explains that the electronegativity of X = Cl/Br influences the magnitude of inversion barrier energy of each of the aziridine compounds under investigation. The variation of substituents on the ring C-atom also has a direct influence on the inversion barrier.

For a particular alkyl/aryl substituent, on changing 'X' from 'Cl' to 'Br' the barrier energy decreases in every case. Thus, as electronegativity decreases the barrier energy decreases.

For X = Cl, the barrier energy increases in the following order:

Trimethyl < Ph < Me < Et < ^{i}Pr

Again, when X = Br, the barrier energy increases in the following order:

Trimethyl < Et < Me < Ph < ^{i}Pr

All the chloro-aziridine compounds have an activation energy value greater than 23 kcal/mol. The result suggests that the corresponding invertomers could be isolated. But for bromo-aziridine compounds the activation energy is not that high suggesting the isolation of invertomers might not be as easy as that of the chloroaziridines.

The Wigner expression, $\chi(T) = 1 + 1/24\ (h\omega/kT)^2$, gives a temperature dependent relation for the transmission coefficient in terms of the single frequency (ω) of the transition structure (Table-2). The calculated transmission coefficient for all the compounds under investigation is unity.

The rate of racemization, [ln (k)] was calculated at different temperatures (ranging from 273-373 K) and the results were plotted against (1/T). Figs. 3 and 4 shows the variation of ln (k) against (1/T) for substituted chloro-aziridine and bromo-aziridine compounds at different temperatures. The graphs show a linear variation of rate with change in temperatures for all the compounds under investigations. As expected the rate of N-inversion for all the compound increases with increase in temperature but the rate is much higher for Br-aziridine compounds compared to Cl-aziridine compounds.

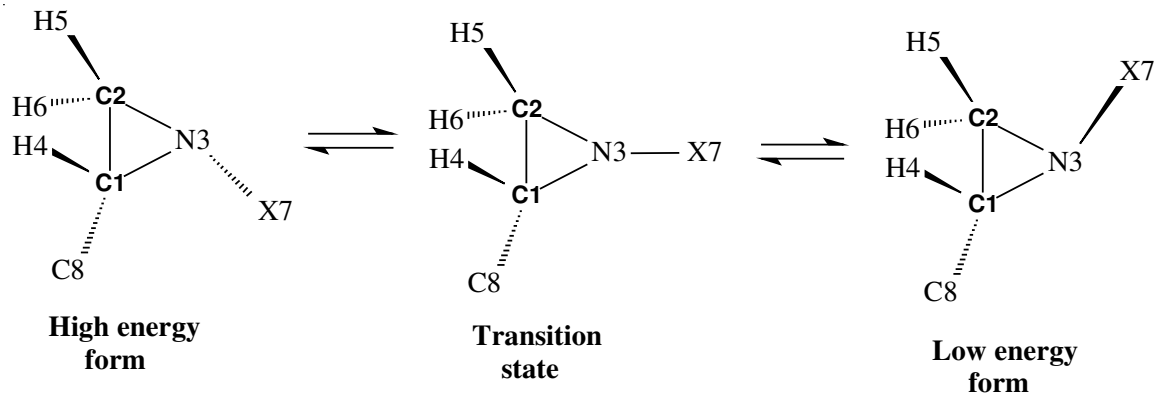


Fig. 2. Pictorial representation of nitrogen inversion in a general aziridine molecule with atom labels

TABLE-1
CALCULATED GEOMETRICAL PARAMETERS OF DIFFERENT AZIRIDINE TYPE COMPOUNDS (BOTH ENERGY FORMS), THEIR PLANAR-SHAPED TRANSITION STATE STRUCTURES (TS) FOR N-INVERSION CALCULATED BY THE B3LYP METHOD

	1-Bromo-2-methyl-aziridine (C6)			1-Chloro-2-methyl-aziridine (C1)		
Geometrical parameters	Low energy form	TS	High energy form	Low energy form	TS	High energy form
R(C1,C2)/Å	1.4906	1.5621	1.491	1.4896	1.5728	1.4897
R(C1,N3)	1.4791	1.3997	1.4827	1.4812	1.3952	1.4887
R(C2,N3)	1.4783	1.3983	1.4788	1.4813	1.3928	1.4803
R(N3,X7)	1.9337	1.8346	1.9359	1.7931	1.7015	1.7946
A(C2,C1,C8)/°	122.770	120.358	121.857	123.270	120.627	121.953
A(C1,N3,X7)	114.060	146.395	116.691	113.415	146.102	115.532
A(C2,N3,X7)	113.648	145.646	114.388	112.903	145.160	113.631
D(C8,C1,N3,X7)/°	-140.684	-69.048	5.728	-140.837	-69.689	6.390
D(H5,C2,N3,X7)	2.552	-77.284	-137.243	3.058	-76.682	-138.335
D(C8,C1,C2,H5)	149.739	142.495	145.675	150.052	142.728	145.918
D(H4,C1,C2,H5)	-1.612	-1.134	-3.999	-1.552	-1.030	-4.133
	1-Bromo-2-ethyl-aziridine (C7)			1-Chloro-2-ethyl-aziridine (C2)		
R(C1,C2) / Å	1.491	1.564	1.492	1.490	1.574	1.490
R(C1,N3)	1.478	1.398	1.481	1.480	1.394	1.487
R(C2,N3)	1.479	1.397	1.479	1.481	1.392	1.480
R(N3,X7)	1.933	1.834	2.649	1.794	1.702	2.655
A(C2,C1,C8) / °	122.575	120.314	140.864	123.272	120.514	142.961
A(C1,N3,X7)	114.079	146.340	28.182	113.369	146.097	28.083
A(C2,N3,X7)	113.526	145.449	73.027	112.950	145.052	72.656
D(C8,C1,N3,X7)/°	-141.155	-68.234	28.203	-140.887	-69.857	29.864
D(H5,C2,N3,X7)	2.587	-78.197	142.302	3.191	-76.819	142.470
D(H4,C1,C2,H5)	-1.277	-1.023	-3.801	-1.284	-0.840	-3.894
D(C8,C1,C2,H5)	149.422	142.249	176.047	149.629	142.261	173.130
	1-Bromo-2-isopropyl-aziridine (C8)			1-Chloro-2-isopropyl-aziridine (C3)		
R(C1,C2) / Å	1.4917	1.5631	1.4883	1.4911	1.5739	1.4886
R(C1,N3)	1.476	1.4008	1.4854	1.4792	1.3969	1.4893
R(C2,N3)	1.4769	1.399	1.4807	1.4788	1.3933	1.4802
R(N3,X7)	1.9278	1.8359	2.6632	1.7935	1.7028	2.6696
A(C2,C1,C8) / °	126.229	123.202	97.150	126.349	123.325	97.026
A(C1,N3,X7)	114.859	146.795	27.920	113.719	146.613	27.781
A(C2,N3,X7)	114.162	145.048	72.932	113.290	144.538	72.481
D(C8,C1,N3,X7)/°	-136.736	-63.542	-19.226	-137.512	-64.955	-18.416
D(H5,C2,N3,X7)	0.5021	-80.2059	141.6489	1.9649	-79.0984	142.0738
D(H4,C1,C2,H5)	-2.0455	-1.5155	-4.5481	-2.211	-1.4007	-4.4284
D(C8,C1,C2,H5)	149.555	141.964	159.918	148.948	141.959	160.318
	1-Bromo-2-phenyl-aziridine (C9)			1-Chloro-2-phenyl-aziridine (C4)		
R(C1,C2) / Å	1.496	1.579	1.487	1.498	1.588	1.487
R(C1,N3)	1.484	1.396	1.501	1.483	1.392	1.506
R(C2,N3)	1.471	1.394	1.477	1.470	1.389	1.478
R(N3,X7)	1.926	1.842	1.933	1.789	1.707	1.790
A(C2,C1,C8)/°	123.144	119.643	124.029	124.080	120.367	123.954
A(C1,N3,X7)	113.754	146.023	115.240	113.515	145.504	115.065
A(C2,N3,X7)	112.951	144.780	113.106	113.640	144.743	112.962
D(C8,C1,N3,X7)/°	-141.655	-68.3060	9.4193	-139.848	-69.317	9.427
D(H5,C2,N3,X7)	1.989	-80.239	-140.112	2.307	-78.605	-139.888
D(H4,C1,C2,H5)	-2.132	-0.357	-6.218	-2.172	-0.255	-6.466
D(C8,C1,C2,H5)	147.515	140.893	145.492	147.397	141.512	145.581
	1-Bromo-2,2,3-trimethyl-aziridine (C10)			1-Chloro-2,2,3-trimethyl-aziridine (C5)		
R(C1,C2)/Å	1.503	1.581	1.500	1.502	1.593	1.498
R(C1,N3)	1.478	1.401	1.490	1.479	1.395	1.495
R(C2,N3)	1.487	1.407	1.492	1.494	1.402	1.499
R(N3,X7)	1.931	1.847	1.932	1.796	1.716	2.652
A(C2,C1,C8)/°	126.504	123.333	124.960	126.716	123.467	146.729
A(C1,N3,X7)	116.115	145.194	116.970	115.070	144.750	28.236
A(C2,N3,X7)	118.465	146.000	117.212	117.305	145.635	74.259
D(C8,C1,N3,X7)/°	-131.804	-63.614	6.571	-132.586	-64.538	29.651
D(C5,C2,N3,X7)	0.733	-80.531	-141.056	1.439	-79.314	138.515
D(H4,C1,C2,C5)	-4.063	0.124	-1.071	-4.830	0.572	-1.324
D(C8,C1,C2,C5)	146.685	143.520	149.001	145.993	144.137	176.288

TABLE-2
CALCULATED ENERGY VALUES (B3LYP), ln (k), ARRHENIUS PARAMETERS AND IMAGINARY FREQUENCY (ω) FOR N-INVERSION PROCESS

Substrate	$\Delta E^{\#}$ (Kcal/mol)	$\Delta H^{\#}$ (Kcal/mol)	$\Delta G^{\#}$ (Kcal/mol)	ln (k) (s^{-1})	E_a (Kcal/mol)	A (10^{12} s^{-1})	ω (cm^{-1}) (-ve)
1-Chloro-2-methyl-aziridine (C1)	24.529	24.529	24.932	-12.664	25.121	3.142	391.107
1-Chloro-2-ethyl-aziridine (C2)	24.577	24.577	24.947	-12.689	25.169	3.321	388.455
1-Chloro-2-isopropyl-aziridine (C3)	24.868	24.868	25.121	-12.982	25.459	4.054	382.774
1-Chloro-2-phenyl-aziridine (C4)	23.466	23.466	24.058	-11.186	24.058	2.288	311.937
1-Chloro-2,2,3-trimethyl-aziridine (C5)	22.771	22.770	23.140	-9.636	23.362	3.328	326.654
1-Bromo-2-methyl-aziridine (C6)	21.092	21.092	21.597	-7.029	21.684	2.646	339.345
1-Bromo-2-ethyl-aziridine (C7)	20.552	20.552	21.296	-6.521	21.144	1.767	331.408
1-Bromo-2-isopropyl-aziridine (C8)	22.251	22.251	22.636	-8.784	22.843	2.565	335.681
1-Bromo-2-phenyl-aziridine (C9)	21.447	21.448	21.706	-7.214	22.040	4.007	368.928
1-Bromo-2,2,3-trimethyl-aziridine (C10)	19.464	19.465	20.011	-4.351	20.057	2.466	272.542

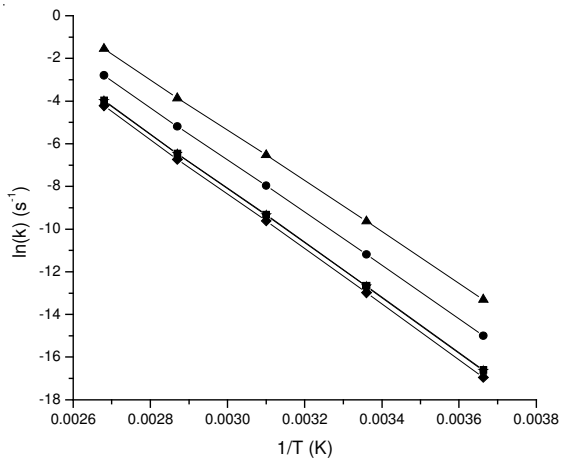


Fig. 3. Activation energy for N-inversion *versus* ln (k) (Arrhenius plot), for chloroaziridine type compounds: C1 (■), C2 (*), C3 (◆), C4 (●), C5 (▲)

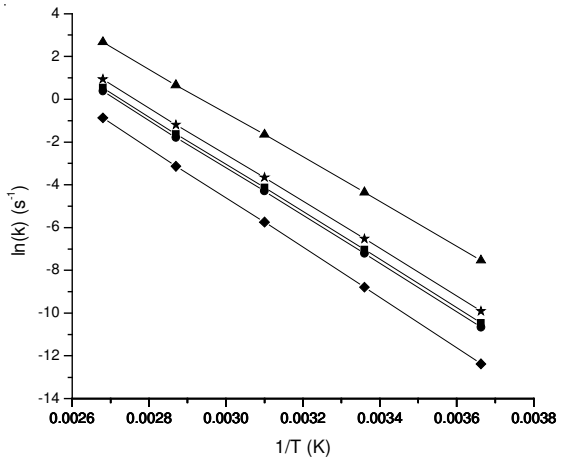


Fig. 4. Activation energy for N-inversion *versus* ln (k) (Arrhenius plot), for bromoaziridine type compounds: C6 (▲), C7 (*), C8 (◆), C9 (●), C10 (▲)

Conclusion

Using the density function theory (B3LYP) the structural geometrical parameters of various substituted aziridine compounds in equilibrium state and planar-shaped transition structure along with the corresponding imaginary frequencies and kinetic parameters towards N-inversion were determined. In planarization to N-inversion, there is an increase in bond angles within the ring and shortening of the angles between the ring and the substituent on C-atoms. This is accompanied by decrease in C-N and N-X bond lengths and increase in C-C bond lengths. For all the bromo and chloro aziridine compounds under investigation, the rate of N-inversion is the slowest when the substituent is isopropyl and fastest when the substituent is trimethyl for various experimental temperatures. The linearity of the ln k *versus* 1/T graph supports the reliability of the calculated energetic and kinetic parameters. For a particular substitution in the aziridine ring, the rate of N-inversion increases on decreasing the electronegativity of the substituent on N-atom of the heterocyclic ring. The calculated results quantitatively shows that incorporation of substitution in the C-atom of the aziridine ring and even on N-atom could substantially increase the relatively low energy barrier to pyramidal N-inversion and thus lead to the isolation of chiral aziridine compounds.

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