

Ring opening fragmentations of ionized cyclohexylamines

Sung-Seen Choi^{a,*}, Hun-Young So^b

^a Department of Applied Chemistry, Sejong University, 98 Koonja-dong, Kwangjin-gu, Seoul 143-747, Republic of Korea

^b Korea Research Institute of Standards and Science, P.O. Box 102, Yuseong, Daejeon 305-600, Republic of Korea

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Abstract

Fragmentations of cyclohexylamine and dicyclohexylamine ions were studied using FTMS. Fragmentations of the molecular ions were initiated by the ring opening of cyclohexyl group to form the distonic molecular ions. The structures of fragment ions were determined by rearranging the distonic molecular ion. The major fragment ions were found to be $X\text{-HC=NH}_2^+$ and $c\text{-C}_6\text{H}_{11}\text{-HN=CH-X}^+$ for cyclohexylamine and dicyclohexylamine, respectively, where X is CH=CH_2 and $\text{CH}_2\text{CH=CH}_2$. The formations of $\text{CH}_2\text{=CHCH=NH}_2^+$ and $c\text{-C}_6\text{H}_{11}\text{-HN=CHCH=CH}_2^+$ for cyclohexylamine and dicyclohexylamine, respectively, were more favorable than the formations of the other fragment ions because of the easy rearrangement of the distonic molecular ions. Experimental and calculation results suggest that the formations of fragment ions with acyclic structures were more favorable than those with cyclic ones. It was also found that for dicyclohexylamine the formations of fragment ions with cyclohexyl group, such as $c\text{-C}_6\text{H}_{11}\text{-HN=CH-X}^+$ were more favorable than those without cyclohexyl group, such as $X\text{-HC=NH}_2^+$.

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1. Introduction

Fourier transform mass spectrometry (FTMS) has been widely used in the study of gas-phase chemistry [1–5]. Its capability of trapping ions and high resolution has motivated researchers to utilize FTMS as one of the premier methods for exploring gas-phase ion–molecule chemistry. Molecules with specific functional groups undergo typical fragmentation patterns, which can be used to obtain structural information. For example, the mass spectra of alcohols and ethers show prominent ions of general formula with $\text{C}_n\text{H}_{2n}\text{O}^{\bullet+}$ [6,7]. Ionized alcohols are fragmented and rearranged as a water molecule is lost [8,9]. Blanc and Gülarar [10] studied the formation of ring structure by rearrangement of aliphatic diols having general formula of $\text{HO(CH}_2)_n\text{OH}$ with $n=2\text{--}11$. They reported that a five-membered ring involving oxygen was formed by loss of wa-

ter molecule from $\text{HO(CH}_2)_4\text{OH}^{\bullet+}$, and that cyclohexene ion was also formed by loss of two water molecules from $\text{HO(CH}_2)_6\text{OH}^{\bullet+}$.

Fujii and Kitai [11] studied surface ionization of diamines and aminoalcohols. They reported that $[M - \text{H}]^+$, $\text{C}_2\text{H}_6\text{N}^+$, and CH_4N^+ ions were distinctive for ethylenediamine as well as ethanolamine. Audier et al. [12] studied the formation of cyclic diols by chemically ionizing a bifunctional organic molecule, $\text{HO(CH}_2)_4\text{NH}_2$. They proposed that the protonated tetrahydrofuran is formed from $\text{HO(CH}_2)_4\text{NH}_3^+$ by loss of NH_3 , while protonated pyrrolidine is formed from $\text{H}_2\text{N(CH}_2)_4\text{OH}_2^+$ by loss of H_2O . Bowen [13] reviewed the chemistry of $\text{C}_n\text{H}_{2n+2}\text{N}^{\bullet+}$ ions, which were dissociated into various smaller fragment ions by loss of H_2 , alkyl groups, NH_3 , primary and secondary amines, alkanes, or alkenes. Distonic ions involving nitrogen [14] or oxygen [15–17] have been studied. Bjornholm et al. [14] studied the characteristic reactions of distonic radical ions of derivatives of $\bullet\text{CH}_2\text{CH}_2\text{NH}_3^+$. One of the typical fragmentations of derivatives of $\bullet\text{CH}_2\text{CH}_2\text{NH}_3^+$ is the loss of alkyl radical.

* Corresponding author. Tel.: +82 2 3408 3815; fax: +82 2 462 9954.

E-mail address: sschoi@sejong.ac.kr (S.-S. Choi).

The mass spectra of functionalized cyclic compounds commonly show a ring-cleavage decomposition and the cleavage of a bond in a cyclic structure produces distonic ions [18].

In the present work, we investigated fragmentations of ionized cyclohexylamine and dicyclohexylamine by varying experimental conditions, such as sample pressure and ion trapping time. This paper focuses on the changes in fragmentation patterns due to the ring opening of cyclohexyl group and distonic molecular ions. The rearrangements of molecular ions and the structures of distonic molecular ions were investigated by means of AM1 semiempirical calculations as well as experiments.

2. Experimental

All the experiments were carried out on an Extrel FTMS 2000 Fourier transform ion cyclotron resonance (FT/ICR) mass spectrometer. The instrument is equipped with two diffusion pumps attached to dual ion trapping cells aligned collinearly in a superconducting magnet of 3.1 T. The cells are 2 in. cubic and a conductance limit is shared between the two cells. The nominal value of background pressure was lower than 1×10^{-8} Torr. Samples were introduced into the cell through a heated batch inlet.

Cyclohexylamine and dicyclohexylamine obtained from Aldrich Co. were used without further purification. The heats of formation of ions, which were not available from literature [19], were calculated by the AM1 semiempirical method to investigate the stabilities of observed ions. The calculation results were used to elucidate the heats of reaction to understand fragmentations of cyclohexylamine and dicyclohexylamine. The structures of distonic molecular ions of cyclohexylamine and dicyclohexylamine were calculated to explain the favorable conditions for fragmentations in accordance with the structures.

3. Results and discussion

3.1. Fragmentation of cyclohexylamine

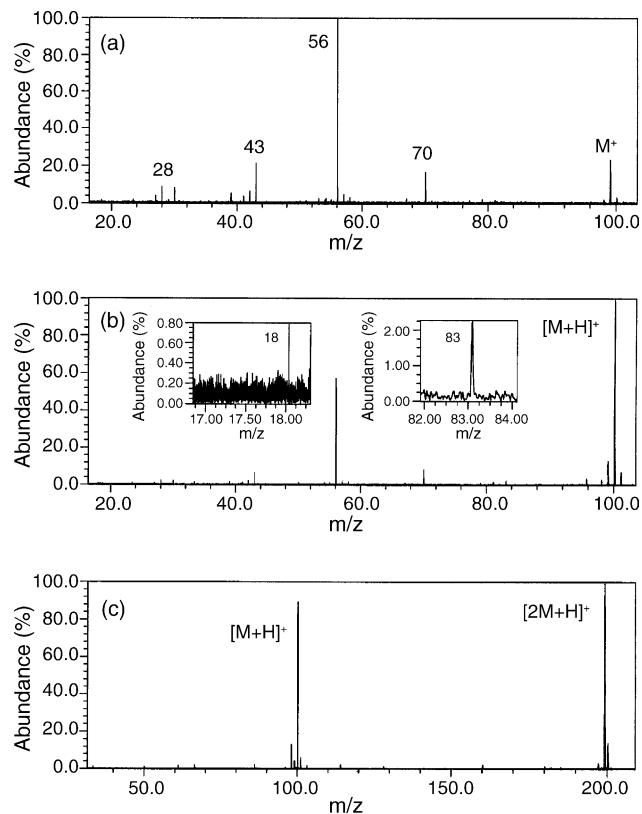
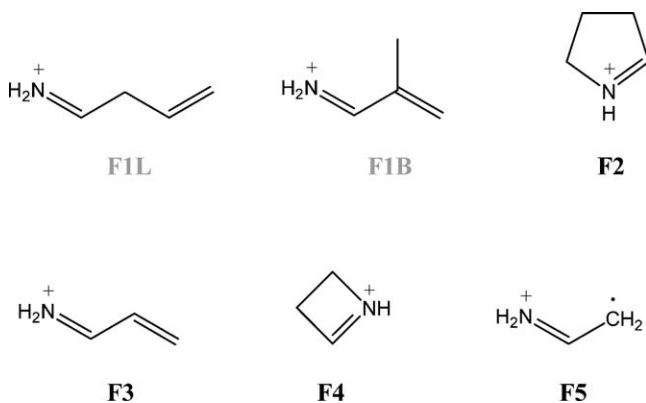
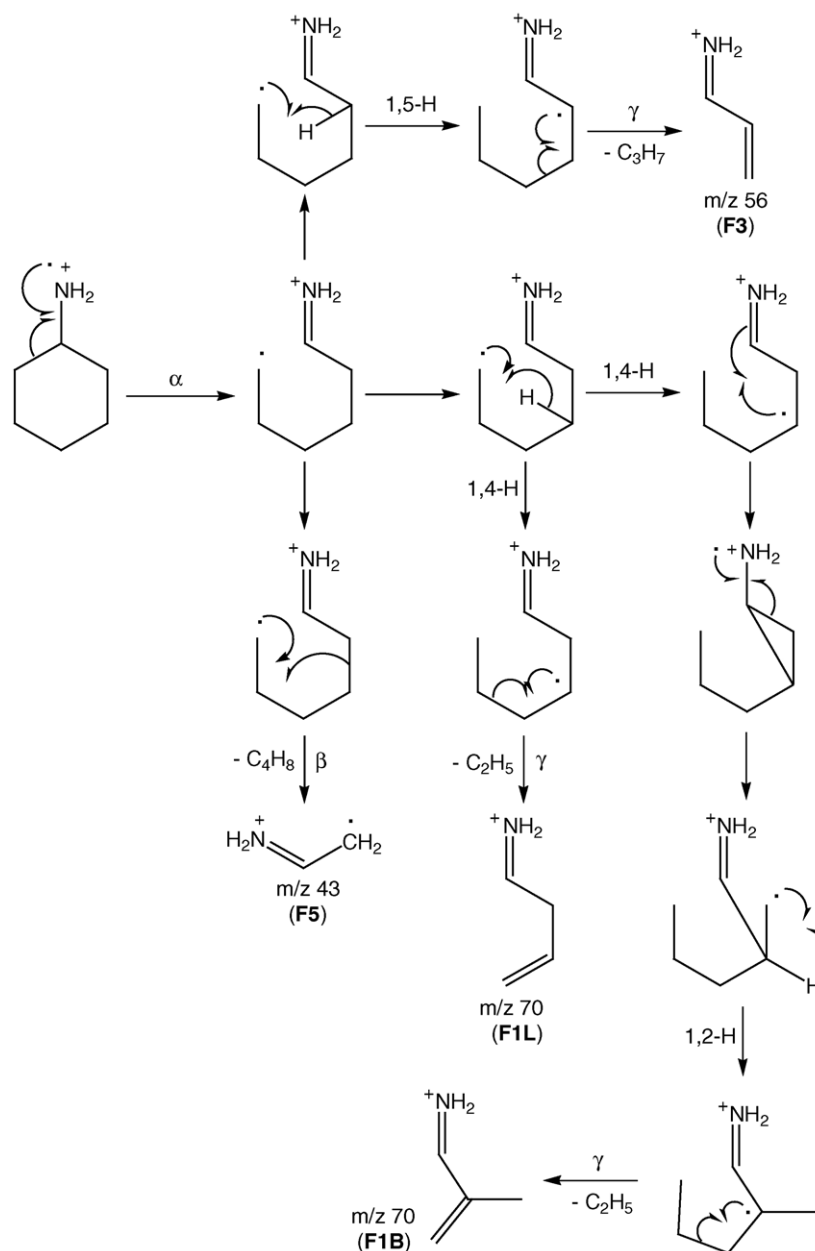


Fig. 1. Electron impact ionization mass spectra of cyclohexylamine at 50 eV of the electron impact energy. The sample pressure and ion trapping time are: (a) 1.8×10^{-6} Torr/1 ms; (b) 6.0×10^{-6} Torr/50 ms; (c) 6.0×10^{-6} Torr/10 s.

Major fragment ions with more than 10% of the relative ion abundance at a short ion trapping time are m/z 43, 56, and 70 assigned to $C_2H_5N^+$, $C_3H_6N^+$, and $C_4H_8N^+$, respectively, as shown in Fig. 1(a). One can consider both of acyclic (F1L/F1B and F3) and cyclic (F2 and F4) structures as the plausible structures of $C_4H_8N^+$ and $C_3H_6N^+$. Ionized amine compounds having a cyclic group (for example, cyclohexyl or cyclopentyl) are rearranged to their distonic ions and the cyclic group is decomposed by α -cleavage [18]. For ethylcyclohexylamine, the distonic molecular ion is produced by α -cleavage of the ionized molecule and $C_2H_5-NH=CHCH=CH_2^+$ is generated by 1,2-hydrogen shift and α -cleavage [18]. In this study, the ionized cyclohexylamine was rearranged to the distonic ion by α -cleavage as shown in Scheme 1. We were able to form F1L/F1B and F3 from the distonic molecular ion generated by α -cleavage of the ionized cyclohexylamine.

F1L/F1B and F3 were formed from the distonic molecular ion by the hydrogen shift through five- and six-membered rings, respectively. The distonic molecular ion with six-membered ring ($\Delta H_f = 724$ kJ/mol) was more stable than that with five-membered one ($\Delta H_f = 734$ kJ/mol) by 10 kJ/mol. The distance between C1 and C5 was 2.890 Å in the distonic molecular ion with six-membered ring, while that be-



Scheme 1. Fragmentation of ionized cyclohexylamine.

tween **C1** and **C4** was 2.915 \AA in the distonic molecular ion with five-membered one. Thus, the formation of **F3** was more favorable than that of **F1L/F1B** according to the stabilities of intermediate structures and the distances between methylene carbons. **F3** was formed by 1,2-hydrogen shift and γ -cleavage from the distonic molecular ion. **F1L** was formed by 1,4-hydrogen shift and γ -cleavage, while **F1B** was formed through the intermediate having a trigonal ring and 1,2-hydrogen shift (Scheme 1). The m/z 43 in the mass spectrum is assigned to **F5**, which was also formed from the distonic molecular ion as shown in Scheme 1. **F5** was formed by the β -cleavage and loss of cyclobutane from the distonic molecular ion.

If the $C_4H_8N^+$ and $C_3H_6N^+$ are cyclic, such as **F2** and **F4**, the $C_4H_8N^+$ will be formed more abundantly than the $C_3H_6N^+$ according to the heats of reaction for fragmentations as listed in Table 1. The AM1 calculation results show that the formation of cyclic **F2** is much more favorable than cyclic **F4** by 162 kJ/mol as shown in Table 1. However, the experimental results in Fig. 1(a) show that the $C_3H_6N^+$ is observed more abundantly than the $C_4H_8N^+$, which contradicts the expectation based on the cyclic structures. If the $C_4H_8N^+$ and $C_3H_6N^+$ have acyclic structures, such as **F1L/F1B** and **F3**, the calculation results for heats of reaction are consistent with the experimental observations. The calculation results show that the formation of acyclic $C_3H_6N^+$ (**F3**) is more stable than

Table 1
Heats of reaction for fragmentation of cyclohexylamine

Reaction	ΔH (kJ/mol)
$c\text{-C}_6\text{H}_{11}\text{-NH}_2^{\bullet+}$ (712) \rightarrow $\bullet\text{CH}_2(\text{CH}_2)_4\text{CH}=\text{NH}_2^+$ (724/734) ^a	12/22
$c\text{-C}_6\text{H}_{11}\text{-NH}_2^{\bullet+}$ (712) \rightarrow F1L (732) + $\text{CH}_3\text{CH}_2\bullet$ (76)	96
$c\text{-C}_6\text{H}_{11}\text{-NH}_2^{\bullet+}$ (712) \rightarrow F1B (748) + $\text{CH}_3\text{CH}_2\bullet$ (76)	112
$c\text{-C}_6\text{H}_{11}\text{-NH}_2^{\bullet+}$ (712) \rightarrow F2 (686) + $\text{CH}_3\text{CH}_2\bullet$ (76)	50
$c\text{-C}_6\text{H}_{11}\text{-NH}_2^{\bullet+}$ (712) \rightarrow F3 (756) + $\text{CH}_3\text{CH}_2\text{CH}_2\bullet$ (48)	92
$c\text{-C}_6\text{H}_{11}\text{-NH}_2^{\bullet+}$ (712) \rightarrow F4 (876) + $\text{CH}_3\text{CH}_2\text{CH}_2\bullet$ (48)	212
$c\text{-C}_6\text{H}_{11}\text{-NH}_2^{\bullet+}$ (712) \rightarrow F5 (820) + $c\text{-C}_4\text{H}_8$ (27)	135
$c\text{-C}_6\text{H}_{11}\text{-NH}_2^{\bullet+}$ (712) \rightarrow $c\text{-C}_6\text{H}_{11}^+$ (732) + $\text{H}_2\text{N}\bullet$ (386)	406
$c\text{-C}_6\text{H}_{11}\text{-NH}_3^+$ (482) \rightarrow NH_4^+ (631) + $c\text{-C}_6\text{H}_{10}$ (−5)	144
$c\text{-C}_6\text{H}_{11}\text{-NH}_3^+$ (482) \rightarrow $c\text{-C}_6\text{H}_{11}^+$ (732) + NH_3 (−46)	204
$c\text{-C}_6\text{H}_{11}\text{-NH}_3^+$ (482) \rightarrow $\text{NH}_3^{\bullet+}$ (877) + $c\text{-C}_6\text{H}_{11}\bullet$ (−27)	368
F1L/F1B (732/748) \rightarrow $c\text{-C}_2\text{H}_4\text{N}^+$ (1026) + $\text{H}_2\text{C}=\text{CH}_2$ (52)	346/330
F1L/F1B (732/748) \rightarrow $\text{H}_2\text{C}=\text{NH}_2^+$ (745) + $\text{HC}\equiv\text{CCH}_3$ (187)	200/184
F1L/F1B (732/748) \rightarrow $\text{HC}\equiv\text{NH}^+$ (955) + $\text{H}_2\text{C}=\text{CHCH}_3$ (20)	243/227
F3 (756) \rightarrow $\text{H}_2\text{C}=\text{NH}_2^+$ (745) + $\text{HC}\equiv\text{CH}$ (228)	217
F3 (756) \rightarrow $\text{HC}\equiv\text{NH}^+$ (955) + $\text{H}_2\text{C}=\text{CH}_2$ (52)	251

Values in parentheses are heats of formation in kJ/mol.

^a Distonic molecular ion: ΔH_f (six-membered ring) = 724 kJ/mol and ΔH_f (five-membered ring) = 734 kJ/mol.

that of acyclic $\text{C}_4\text{H}_8\text{N}^+$ (**F1L/F1B**) by 4/20 kJ/mol, respectively, as listed in Table 1. It is interesting that the difference in the heats of formation for **F1L/F1B** and **F3** is not big, while the difference between the relative abundances of $\text{C}_4\text{H}_8\text{N}^+$ and $\text{C}_3\text{H}_6\text{N}^+$ is big. The relative ion abundances of $\text{C}_4\text{H}_8\text{N}^+$ and $\text{C}_3\text{H}_6\text{N}^+$ are 16.6 and 100.0%, respectively, as shown in Fig. 1(a). Thus, the difference in relative abundances of $\text{C}_4\text{H}_8\text{N}^+$ and $\text{C}_3\text{H}_6\text{N}^+$ cannot be sufficiently explained only with the heats of reaction for fragmentations, but this difference can be explained by the degree of ease with which the distonic molecular ions can be rearranged as discussed previously.

F1L/F1B and **F3** were further dissociated into smaller fragment ions by loss of some neutral molecules. The **F1L/F1B** were dissociated into $\text{C}_2\text{H}_4\text{N}^+$ (m/z 42), CH_4N^+ (m/z 30), and CH_2N^+ (m/z 28) by loss of C_2H_4 , C_3H_4 , and C_3H_6 , respectively. **F3** was also dissociated into CH_4N^+ and CH_2N^+ by loss of C_2H_2 and C_2H_4 , respectively. These secondary fragment ions of m/z 42, 30, and 28 were observed in the mass spectrum of Fig. 1(a). The heats of reaction for the further fragmentations of **F1L/F1B** and **F3** are listed in Table 1. Since **F1B** has a methyl group, it can be more reasonable to form m/z 30 and 28 from **F1B** not from **F1L**, when the structures of C_3H_4 and C_3H_6 are $\text{HC}\equiv\text{CCH}_3$ and

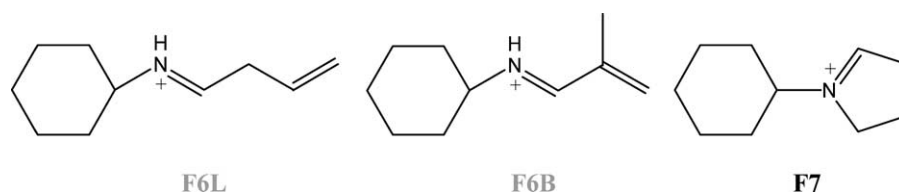
$\text{H}_2\text{C}=\text{CHCH}_3$, respectively. Heats of reactions for the formations of m/z 30 and 28 from **F1B** are also lower than those from **F1L**.

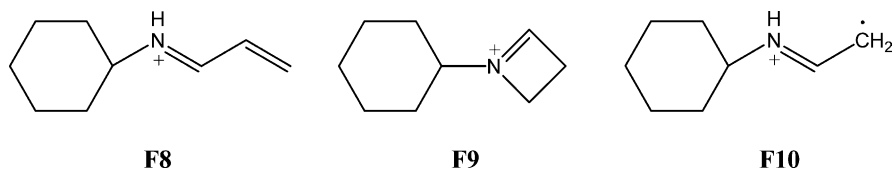
Although it is reasonable to expect that the $\text{C}_6\text{H}_{11}^+$ (m/z 83) to be formed from the molecular ion by direct dissociation of the N–C bond and loss of the NH_2 radical, the m/z 83 peak was not observed at a short ion trapping time as shown in the mass spectrum of Fig. 1(a). The absence of m/z 83 peak in Fig. 1(a) can be also explained with the heats of reaction as listed in Table 1. Major primary fragment ions, such as **F1L/F1B**, **F3**, and **F5** were formed from the distonic molecular ion as discussed above. Heats of reaction for the rearrangements of the ionized molecules to distonic ions with five- and six-membered rings were 22 and 12 kJ/mol, respectively, while that for the formation of m/z 83 from the molecular ion by the direct C–N bond breaking was 406 kJ/mol as listed in Table 1. Thus, the ionized cyclohexylamine was rearranged to the distonic ion but was not dissociated into m/z 83 by the direct C–N bond breaking because of the big difference in the heats of reaction.

The protonated molecule, $[M + \text{H}]^+$, was generated by proton transfer reactions between the product ions and neutral molecules. Proton transfer reactions between product ions and neutral molecules occur often in FTICR cell to form protonated molecules [20]. The $[M + \text{H}]^+$ increased notably, while the smaller fragment ions decreased by increasing the ion trapping time and the sample pressure. If the $[M + \text{H}]^+$ has excess internal energy, it can be further dissociated into the smaller ions. Thus, we were able to dissociate the protonated cyclohexylamine into $\text{NH}_3^{\bullet+}$, NH_4^+ , and $c\text{-C}_6\text{H}_{11}^+$. The NH_4^+ was formed from the $[M + \text{H}]^+$ by loss of cyclohexene, while the $c\text{-C}_6\text{H}_{11}^+$ and $\text{NH}_3^{\bullet+}$ was formed by direct dissociations of the N–C bond. The $c\text{-C}_6\text{H}_{11}^+$ (m/z 83) and NH_4^+ (m/z 18) were observed, but the $\text{NH}_3^{\bullet+}$ (m/z 17) was not observed in the mass spectrum of Fig. 1(b). The formation of $\text{NH}_3^{\bullet+}$ required very high energy as listed in Table 1.

By using the ion trapping capability of ion cyclotron resonance cell in FTMS, cyclohexylamine ion was trapped in the ICR cell for several seconds. One of the resulting mass spectra is shown in Fig. 1(c), which was obtained at 10 s of the ion trapping time. In addition to the peaks of M^+ , $[M - \text{H}]^+$, and $[M + \text{H}]^+$, the $[2M + \text{H}]^+$ was observed with the highest relative abundance. This is the protonated dimer formed by the ion–molecule reaction between the $[M + \text{H}]^+$ and the neutral molecule in the ICR cell.

3.2. Fragmentation of dicyclohexylamine





For the product ions formed by fragmenting ionized dicyclohexylamine, the observed major fragment ions with more than 10% of the relative ion abundance at a short ion trapping time were m/z 56, 138, and 152 as shown in Fig. 2(a). The m/z 138 and 152 were assigned to $C_9H_{16}N^+$ and $C_{10}H_{18}N^+$, respectively, based on the plausible fragmentation paths. The fragmentation also began, when the cyclohexyl ring opened. The molecular distonic ion was formed by the α -cleavage of the ionized molecule. The m/z 138 and 152 were formed from the distonic molecular ion by the hydrogen shift and γ -cleavage as shown in Scheme 2. **F6L** was formed by 1,4-hydrogen shift and γ -cleavage, while **F6B** was formed through the intermediate having a trigonal ring and 1,2-hydrogen shift.

The m/z 152 and 138 can have acyclic (**F6L/F6B** and **F8**, respectively) or cyclic structures (**F7** and **F9**, respectively). The heats of reaction for the fragmentations were calculated to elucidate plausible structures of the fragment ions (Table 2). If the m/z 152 and 138 ions have cyclic

structures, the m/z 152 will be observed more abundantly than the m/z 138, because the formation of **F7** from the molecular ion is much more favorable than that of **F9** by 155 kJ/mol as listed in Table 2. However, the experimental results are contrary to the predictions. Fig. 2(a) shows that the m/z 138 is observed more abundant than the m/z 152. Thus, the structures of m/z 152 and 138 are not cyclic but acyclic.

The heat of reaction for the formation of **F8** was lower than that of **F6L/F6B** by 8/23 kJ/mol, respectively, as listed in Table 2, and the m/z 138 (**F8**) was observed more abundantly than the m/z 152 (**F6L/F6B**) as shown in Fig. 2(a). However, favorable conditions for the formation of **F6L/F6B** cannot be sufficiently explained only with the heats of reaction, because the difference in relative ion abundances of m/z 152 and 138 was very big, while the difference in the heats of reaction for the formations of **F8** and **F6L/F6B** was not big. The relative ion abundances of m/z 152 and 138 were 10.8 and 100.0%, respectively, as shown in Fig. 2(a). The difference in the intermediate structures may be another reason for this abundance. The ionized molecule was rearranged to the distonic ions with five- or six-membered rings. **F6L/F6B** was formed by the 1,4-H shift of five-membered ring, while **F8** was formed by the 1,5-H shift of six-membered one as shown in Scheme 2. The distonic molecular ion with six-membered

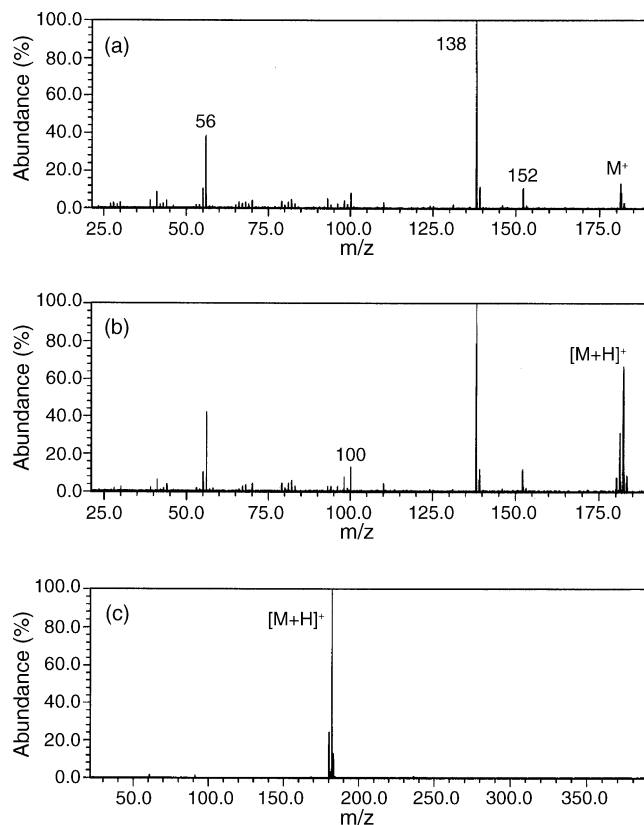


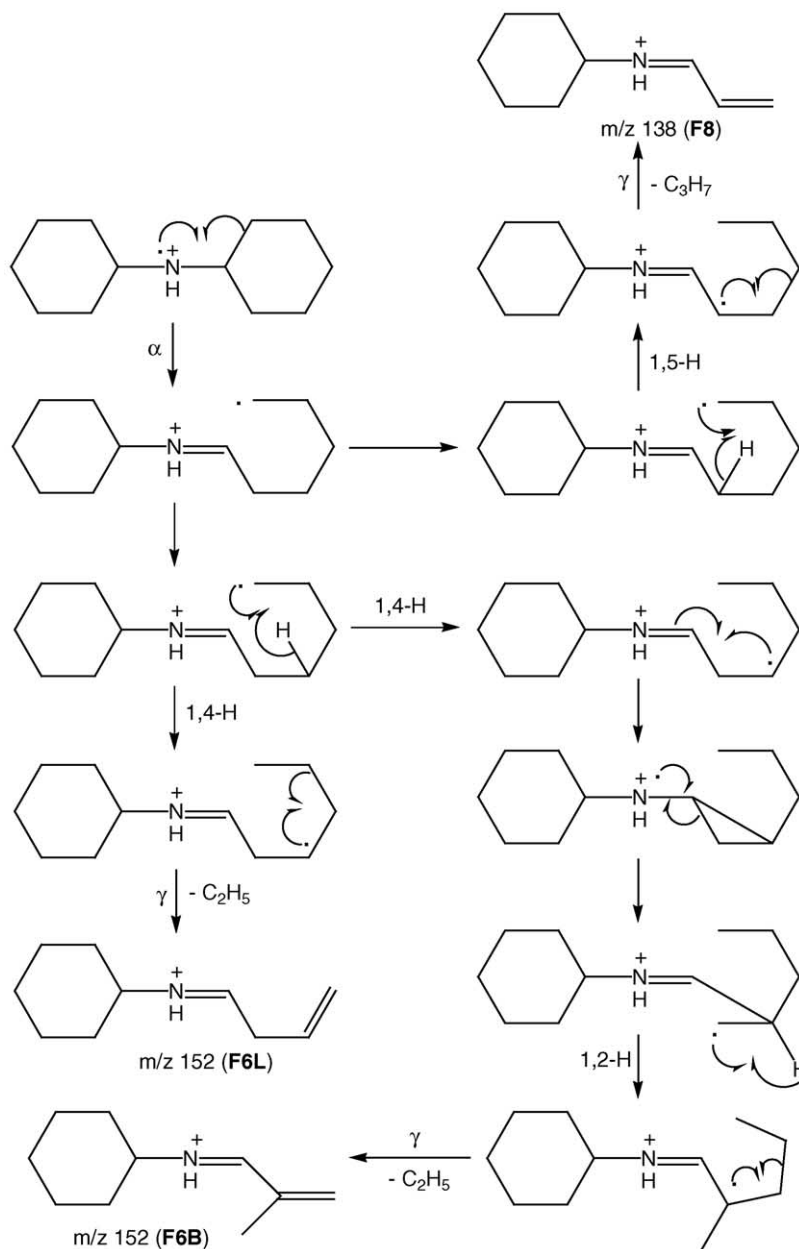
Fig. 2. Electron impact ionization mass spectra of dicyclohexylamine at 50 eV of the electron impact energy. The sample pressure and ion trapping time are: (a) 1.8×10^{-6} Torr/1 ms; (b) 3.1×10^{-6} Torr/50 ms; (c) 3.1×10^{-6} Torr/10 s.

Table 2
Heats of reaction for fragmentation of dicyclohexylamine

Reaction	ΔH (kJ/mol)
$(c-C_6H_{11})_2NH^{+\bullet}$	9/24
$(570) \rightarrow \bullet CH_2(CH_2)_4CH=N(c-C_6H_{11})H^+$ (579/594) ^a	
$(c-C_6H_{11})_2NH^{+\bullet}$ (570) \rightarrow F6L (611) + $CH_3CH_2\bullet$ (76)	117
$(c-C_6H_{11})_2NH^{+\bullet}$ (570) \rightarrow F6B (626) + $CH_3CH_2\bullet$ (76)	132
$(c-C_6H_{11})_2NH^{+\bullet}$ (570) \rightarrow F7 (586) + $CH_3CH_2\bullet$ (76)	92
$(c-C_6H_{11})_2NH^{+\bullet}$ (570) \rightarrow F8 (631) + $CH_3CH_2CH_2\bullet$ (48)	109
$(c-C_6H_{11})_2NH^{+\bullet}$ (570) \rightarrow F9 (769) + $CH_3CH_2CH_2\bullet$ (48)	247
$(c-C_6H_{11})_2NH^{+\bullet}$ (570) \rightarrow F10 (713) + $c-C_4H_8$ (27)	170
$(c-C_6H_{11})_2NH^{+\bullet}$ (570) \rightarrow $c-C_6H_{11}-NH_2^{+\bullet}$	137
(712) + $c-C_6H_{10}$ (-5)	
$(c-C_6H_{11})_2NH^{+\bullet}$ (570) \rightarrow $c-C_6H_{11}^+$	202
(732) + $c-C_6H_{10}-NH\bullet$ (40)	
$(c-C_6H_{11})_2NH_2^+$ (391) \rightarrow $c-C_6H_{11}-NH_3^+$	86
(482) + $c-C_6H_{10}$ (-5)	
$(c-C_6H_{11})_2NH_2^+$ (391) \rightarrow $c-C_6H_{11}^+$	223
(732) + $c-C_6H_{11}-NH_2$ (-118)	
$(c-C_6H_{11})_2NH_2^+$ (391) \rightarrow $c-C_6H_{11}-NH_2^{+\bullet}$	294
(712) + $c-C_6H_{11}\bullet$ (-27)	
F6L (611) \rightarrow F1L (732) + $c-C_5H_7-CH_3$ (-4)	117
F6B (626) \rightarrow F1B (748) + $c-C_5H_7-CH_3$ (-4)	118
F8 (631) \rightarrow F3 (756) + $c-C_5H_7-CH_3$ (-4)	121

Values in parentheses are heats of formation in kJ/mol.

^a Distonic molecular ion: ΔH_f (six-membered ring) = 579 kJ/mol and ΔH_f (five-membered ring) = 594 kJ/mol.



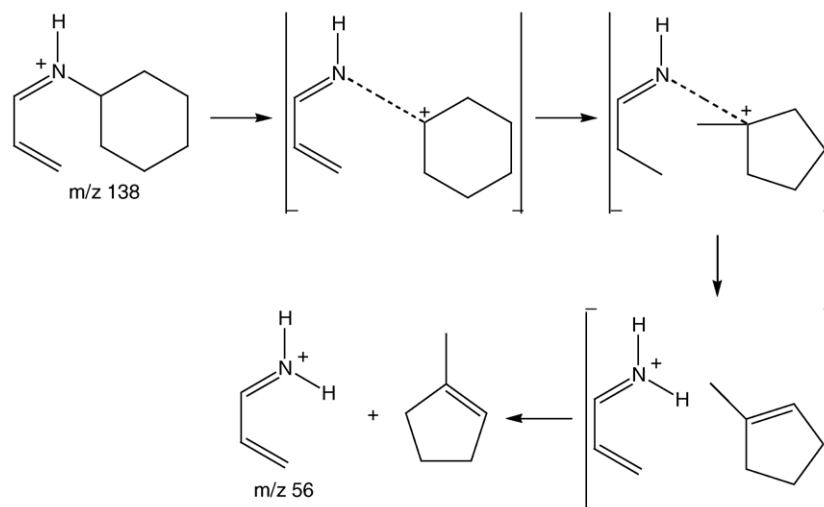
Scheme 2. Fragmentation of ionized dicyclohexylamine.

ring was more stable than that with five-membered one by 15 kJ/mol.

The m/z 125 (**F10**) can be also formed from the distonic molecular ion by rearrangement of the radical part and loss of cyclobutane, but it was hardly observed in the mass spectra as shown in Fig. 2. This is very different from the results of cyclohexylamine, because the m/z 43 (**F5**) was formed from the molecular ion of cyclohexylamine by rearrangement and loss of C_4H_8 . This may be due to the heats of reaction and the difficulty of rearrangement to lose cyclobutane. The difference in heats of reaction for the formations of **F3** and **F5** from cyclohexylamine ion was 43 kJ/mol as listed in Table 1, while that of **F8** and **F10** from dicyclohexylamine ion was 61 kJ/mol

as listed Table 2. **F8** and **F10** were generated through the same intermediate structure. **F8** was formed by migration of hydrogen atom from **C5** to **C1** (1,5-H shift), while **F10** was formed by dissociation of **C4–C5** bond and formation of **C1–C4** bond. The distance between **C1** and hydrogen atom bonded to **C5** was 2.600 Å, while that between **C1** and **C4** was 3.256 Å. Thus, it is hard to form **F10** from the molecular ion because of the big difference in the heats of reaction and the long distance of **C1–C4**.

The m/z 56 and 70 ions were also observed in the mass spectra of dicyclohexylamine, which raises the question of whether they are primary or secondary ions? They can be the secondary ions. If they are secondary ions, they can be formed



Scheme 3. Fragmentation of the m/z 138 ion formed from ionized dicyclohexylamine.

from m/z 138 and 152 and will be observed less abundantly than their precursors, because the formations of secondary ions need more internal energies than those of the primary ions. The m/z 56 and 70 ions were observed less abundantly than the m/z 152 and 138 ions, respectively, in the mass spectra as shown in Fig. 2. The m/z 56 and 70 ions were formed from the m/z 152 and 138 ions, respectively, by loss of 1-methylcyclopentene as shown in Scheme 3. The m/z 56 was observed more abundant than m/z 70, because the precursor of m/z 56 (m/z 138) was much more abundantly than that of m/z 70 (m/z 152).

The $c\text{-C}_6\text{H}_{11}\text{NH}_2^{\bullet+}$ (m/z 99) and $c\text{-C}_6\text{H}_{11}^+$ (m/z 83) were observed as minor fragment ions. It was possible to form the m/z 99 ion by rearrangement and loss of cyclohexene, while the m/z 83 was formed by direct C–N bond breaking. The m/z 99 and 83 were also formed from the protonated molecule, but they were prominently formed from the molecular ion, because the molecular ion had more internal energy than the protonated molecule. The m/z 99 and 83 ions were observed much less than the m/z 138 and 152 ions to form through the distonic molecular ions as discussed previously, because the rearrangements of radical molecular ions into distonic molecular ions were much more favorable than the formations of m/z 99 and 83 by 113–193 kJ/mol.

By increasing the ion trapping time, the protonated molecule was increased as shown in Fig. 2. The protonated dimer of dicyclohexylamine was not observed even at 10 s of the ion trapping time as shown in Fig. 2(c), while the protonated dimer of cyclohexylamine was observed in the mass spectrum as shown in Fig. 1(c). This is attributed to the fact that the two cyclohexyl groups of dicyclohexylamine inhib-

ited the hydrogen bonding between the protonated molecule and the neutral molecule.

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