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«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ  
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»  
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

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## ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

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## MASS SPECTRA OF SOME MONOSUBSTITUTED 1,2-DIAMINOETHANE DERIVATIVES

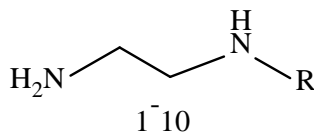
**Abstract.** The mass spectra of monosubstituted 1,2-diaminoethane derivatives are studied and compared. The characteristics of the fragmentation of molecular ions (MI) of 1,2-diaminoethane derivatives are shown and discussed. It was established that the direction of the decomposition reaction of MI depends on the nature of the substituents. It was revealed that under conditions of electrons ionization (EI), the  $\alpha$ - cleavage with the localization of a positive charge on the nitrogen atom is the most important, which leads to the formation of stable ammonium ions.

**Keywords:** 1,2-diaminoethane, mass spectra, ammonium ions, molecular ion, electron ionization.

One of the most promising and rapidly developing areas of organic chemistry is the search for new surface-active substances (surfactants) based on ethylenediamine, mono- and diethanolamine [1-4].

In this regard, the synthesis of ethylenediamine, mono - and diethanolamine derivatives and the study of their properties under conditions of electrons ionization (EI) in mass spectrometry are very relevant.

In the present work, a comparative analysis of the mass spectra of some N-monosubstituted ethylenediamine derivatives (1-10) was carried out in order to identify the features of the basic regularity of molecular ion (MI) fragmentation in IE, depending on the nature of the substituents and allowing reliable mass spectrometric identification. We considered the mass spectra of alkyl, aryl, and trimethoxysilylpropyl-containing derivatives of 1,2-diaminoethane (1-10).



$\text{R} = \text{H}$  (1);  $\text{R} = \text{CH}_3$  (2);  $\text{R} = \text{C}_2\text{H}_5$  (3);  $\text{R} = \text{C}_3\text{H}_7$  (4);  $\text{R} = \text{CH}(\text{CH}_3)_2$  (5);  
 $\text{R} = \text{CH}_2\text{CH}_2\text{NH}_2$  (6);  $\text{R} = \text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$  (7);  $\text{R} = \text{C}_6\text{H}_5$  (8);  
 $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$  (9);  $\text{R} = \text{C}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$  (10);

The amino group has stronger electron-donor properties compared to hydroxyl. The positive mesomeric effect of the nitrogen atom is larger, and the negative inductive effect is smaller than that of the oxygen atom. Therefore, fragmentation processes initiated by the radical center are more characteristic for amines.

In the electron-unexcited state, the charge and the unpaired electron are localized on the nitrogen atom. It should be noted that the intensity of the MI peaks is very low due to the ease of fragmentation processes.

In the case of the absence of the MI peak in mass spectra, the “nitrogen rule” (if the compound contains an even number of nitrogen atoms, its molecular weight is even) [5] allows to accurately set the substances belonging to the class of amines.

The full electrons ionization mass spectra of considered monosubstituted derivatives of 1,2-diaminoethane (1-10) are given in the table 1.

Table 1 – Mass spectra of monosubstituted alkyl- and aryl derivatives of 1,2-diaminoethane

No.	Name of compound	Mass spectrum, m/z ( $I_{relative}$ , %)
1	1,2-diaminoethane	$M^{+}$ 60 (7), 59 (6,5), 44 (4), 43 (15), 42 (12,5), 41 (5), 40 (2,5), 31 (3), 30 (100), 29 (3), 28 (19,5), 27 (3).
2	N-Methylethan-1,2-diamine	$M^{+}$ 74 (5,5), 45 (5), 44 (100), 43 (6), 42 (11), 41 (3), 30 (19), 29 (2), 28 (10,5), 27 (3), 15 (3,5).
3	N-Ethylethan-1,2-diamine	$M^{+}$ 88 (3), 59 (4,5), 58 (100), 56 (3), 44 (13), 43 (3), 42 (6), 41 (2), 30 (79), 29 (8), 28 (9), 15 (2,5).
4	N-Propylethan-1,2-diamine	$M^{+}$ 102 (2,5), 73 (8,5), 72 (100), 70 (2), 58 (3), 56 (4,5), 44 (39,5), 43 (27), 42 (12), 41 (17), 39 (3,5), 30 (83), 28 (13), 27 (7), 18 (2,5).
5	N-Isopropylethan-1,2-diamine	$M^{+}$ 102 (0,5), 73 (3), 72 (57), 70 (3), 58 (10), 56 (2,5), 44 (24), 43 (15), 42 (7), 41 (9), 39 (2,5), 30 (100), 28 (7,5), 27 (5,5), 15 (2).
6	N-(2-Aminoethyl)ethane-1,2-diamine	$M^{+}$ 103 (0,3), 74 (4), 73 (64), 57 (2), 56 (10,5), 45 (3,5), 44 (100), 43 (8), 42 (12), 41 (3), 30 (20), 29 (2), 28 (7,5), 27 (2), 18 (3).
7	N,N-Bis(aminoethyl)ethane-1,2-diamine	$M^{+}$ 146 (ab.), 142 (7), 125 (2), 116 (10,5), 112 (2), 100 (2,5), 99 (20), 98 (9,5), 97 (8), 87 (4), 86 (3), 85 (6), 84 (2), 83 (2), 74 (3), 73 (41), 71 (3), 70 (13), 69 (2), 68 (2), 61 (6), 58 (9), 57 (6), 56 (27), 55 (3), 54 (2), 45 (4), 44 (100), 43 (9), 42 (16,5), 41 (4), 30 (26,5), 29 (5,5), 28 (12), 27 (3), 18 (3).
8	N-Phenylethan-1,2-diamine	$M^{+}$ 136 (15), 107 (20), 106 (100), 104 (4), 79 (14,5), 78 (6), 77 (26), 65 (3), 52 (3), 51 (13,5), 50 (4), 42 (2), 39 (4,5), 30 (20), 28 (7), 27 (2,5).
9	N-Benzylethan-1,2-diamine	$M^{+}$ 150 (1), 121 (5), 120 (44), 118 (2,5), 106 (6), 29 (9), 91 (100), 89 (2), 77 (2), 65 (8,5), 63 (2), 51 (2,5), 44 (3), 42 (2), 39 (3), 30 (11,5), 28 (3,5).
10	N-[3-(Trimethoxysilyl)propyl]ethane-1,2-diamine	$M^{+}$ 222 (ab.), 193 (4), 192 (27,5), 162 (5), 161 (12,5), 160 (100), 159 (2), 148 (3), 132 (2), 131 (4,5), 130 (30,5), 121 (15,5), 118 (3), 91 (15), 90 (2), 73 (8), 61 (5), 59 (6,5), 44 (19), 43 (5,5), 42 (3), 41 (3), 32 (20), 31 (28,5), 30 (11), 29 (13), 28 (6), 18 (3), 15 (6).

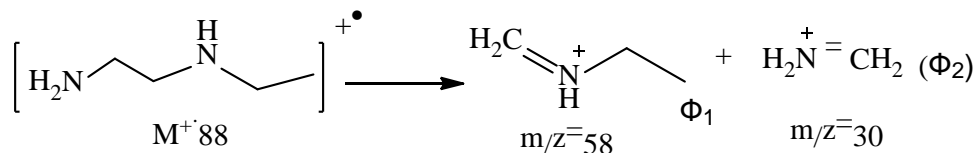
The stability of MI ( $W_{MI}$ ) to EI, as well as the intensity of the main characteristic fragment ions ( $F_1$ - $F_5$ ) from the total ion current and the retention index ( $i_u$ ) are given in the table 2.

Table 2 – Stability of molecular ions ( $W_{MI}$ ) and characteristic fragment ions ( $F_1$ - $F_5$ ) from the total ion current during electrons ionization (EI) of some monosubstituted alkyl- and aryl derivatives of 1,2-diaminoethane (1-10)

№ comp	$W_{MI}$	m/z ( $F_1$ - $F_5$ )					Retention index RI ( $i_u$ ), [7,8]
		$F_1$	$F_2$	$F_3$	$F_4$	$F_5$	
1	3,7	[M-H] <sup>+</sup> 59(3,4)	[M-NH <sub>3</sub> ] <sup>+</sup> 43(7,9)	[M-NH <sub>4</sub> ] <sup>+</sup> 42(6,5)	CH <sub>2</sub> =N <sup>+</sup> H <sub>2</sub> 30(52,6)	H <sub>2</sub> CN 28(10,5)	600÷ 612
2	3,0	CH <sub>3</sub> N <sup>+</sup> H= 44(55,5)	[M-NH <sub>2</sub> ] <sup>+</sup> 43(3,0)	[C <sub>2</sub> H <sub>4</sub> N] <sup>+</sup> 42(6,1)	CH <sub>2</sub> =N <sup>+</sup> H <sub>2</sub> 30(10,2)	H <sub>2</sub> CN 28(5,8)	761
3	1,2	C <sub>2</sub> H <sub>5</sub> N <sup>+</sup> H= 58(39,2)	C <sub>2</sub> H <sub>6</sub> N <sup>+</sup> 44(5,0)	C <sub>2</sub> H <sub>4</sub> N <sup>+</sup> 42(2,3)	CH <sub>2</sub> =N <sup>+</sup> H <sub>2</sub> 30(30,9)	H <sub>2</sub> CN <sup>+</sup> 28(3,4)	860
4	0,7	C <sub>3</sub> H <sub>7</sub> N <sup>+</sup> H= 72(29,8)	C <sub>2</sub> H <sub>6</sub> N <sup>+</sup> 44(11,8)	C <sub>2</sub> H <sub>5</sub> N <sup>+</sup> 43(8,0)	CH <sub>2</sub> =N <sup>+</sup> H <sub>2</sub> 30(24,7)	H <sub>2</sub> CN <sup>+</sup> 28(3,8)	960
5	0,2	i-C <sub>3</sub> H <sub>7</sub> N <sup>+</sup> H= 72(21,9)	C <sub>3</sub> H <sub>8</sub> N <sup>+</sup> 58(3,8)	C <sub>2</sub> H <sub>6</sub> N <sup>+</sup> 44(9,2)	C <sub>2</sub> H <sub>5</sub> N <sup>+</sup> 43(5,7)	CH <sub>2</sub> =N <sup>+</sup> H <sub>2</sub> 30(38,4)	896
6	0,1	C <sub>3</sub> H <sub>8</sub> N <sub>2</sub> <sup>+</sup> 73(25,6)	C <sub>3</sub> H <sub>8</sub> N <sup>+</sup> 56(4,2)	C <sub>2</sub> H <sub>6</sub> N <sup>+</sup> 44(40)	C <sub>2</sub> H <sub>4</sub> N <sup>+</sup> 42(4,8)	CH <sub>2</sub> =N <sup>+</sup> H <sub>2</sub> 30(8)	1025÷ 1028
7	–	[M-4H] <sup>+</sup> 142(1,8)	*C <sub>5</sub> H <sub>14</sub> N <sub>3</sub> <sup>+</sup> 116(2,7)	*C <sub>5</sub> H <sub>11</sub> N <sub>2</sub> <sup>+</sup> 99(5,1) NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> H=C <sup>+</sup> H <sub>2</sub> 73(10,5)	*C <sub>3</sub> H <sub>6</sub> N <sup>+</sup> 56(6,9) *C <sub>2</sub> H <sub>6</sub> N <sup>+</sup> 44(25,6)	*CH <sub>2</sub> =N <sup>+</sup> H <sub>2</sub> 30(6,8)	1501
8	6,0	C <sub>6</sub> H <sub>5</sub> N <sup>+</sup> H= CH <sub>2</sub> 106(37)	C <sub>6</sub> H <sub>7</sub> <sup>+</sup> 79(5,4)	C <sub>6</sub> H <sub>5</sub> <sup>+</sup> 77(9,6)	C <sub>4</sub> H <sub>3</sub> <sup>+</sup> 51(5)	CH <sub>2</sub> =N <sup>+</sup> H <sub>2</sub> 30(7,4)	1329÷ 1335
9	1,4	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> N <sup>+</sup> H= =CH <sub>2</sub> 120(20)	C <sub>6</sub> H <sub>5</sub> CH= N <sup>+</sup> H <sub>2</sub> 106(2,7)	C <sub>7</sub> H <sub>7</sub> <sup>+</sup> 91(45,4)	C <sub>5</sub> H <sub>5</sub> <sup>+</sup> 65(3,8)	CH <sub>2</sub> =N <sup>+</sup> H <sub>2</sub> 30(5)	1434
10	–	[M-CH <sub>2</sub> NH <sub>2</sub> ] <sup>+</sup> 192(6,4)	[M- CH <sub>2</sub> NH <sub>2</sub> ] <sup>+</sup> CH <sub>3</sub> OH 160(23,8)	-O-SiH= CH <sub>2</sub> CH <sub>2</sub> NH= CH <sub>2</sub> 130(7.1)	Si(OCH <sub>3</sub> ) <sup>+</sup> 121(3.7)	-O-SiH=O- 91(3.5)	1396
*F <sub>1</sub> -116, F <sub>1</sub> '-99, F <sub>2</sub> -73, F <sub>3</sub> -56, F <sub>3</sub> '-44, F <sub>5</sub> -30 (7).							

Diamines under EI are fragmented by the same rule as monoamines [6-8]. In mass spectra of monoamines MI peaks are usually little intense or completely absent.

The main process of fragmentation carries out in the case of 1,2-ethylenediamine (1): the  $\alpha$  – cleavage of C – C bond with formation of the ammonium ion  $\text{CH}_2=\text{N}^+\text{H}_2$  at  $m/z$  30 ( $I_{\text{relative}}=100\%$ , Table 1) and with localization of the radical ion center on the nitrogen atom, providing high characteristic mass spectra. The analogous maximum peak in the mass spectra of N-methylethane-1,2-diamine (2) is due to the  $\alpha$  – cleavage of C – C bond leading to the ammonium ion  $\text{H}_3\text{C-NH}^+=\text{CH}_2$  at  $m/z$  44 ( $I_{\text{relative}} = 100\%$ ). The mass spectrum of N-ethylethane-1,2-diamine (3) contains two very intense peaks at  $m/z$  30 and 58. The  $\alpha$ - cleavage of the C – C bond between nitrogen atoms is the main process of fragmentation and at the same time the charge can be localized on the right ( $F_1$ ) and left part ( $F_2$ ) of the molecule:



Moreover, the first fragmentary ion F at  $m/z$  58 is more stable due to the inductive influence of the ethyl radical. In terms of mass spectrometry, N-propylethane-1,2-diamine (4) is similar to N-ethylethane-1,2-diamine (3). The dissociation of the  $\text{C}_1 - \text{C}_2$  bond leads to two characteristic fragmentary ammonium ions  $\text{CH}_3-\text{CH}_2-\text{CH-N}^+\text{H}=\text{CH}_2$  ( $m/z$  72) and  $\text{CH}_2=\text{N}^+\text{H}_2$  ( $m/z$  30).

Comparison of the mass spectra of the isomers of N-propyl-, N-isopropylethane-1,2-diamines (4,5) shows a significant difference in the relative intensity of the main fragments and this fact can be used for mass spectrometric identification of the corresponding isomeric pairs.

During the decomposition reaction of MI of N- (2-aminoethyl) ethane-1,2-diamine (6), the main direction of MI fragmentation is the sequential elimination of the radicals  $\text{CH}_2\text{NH}_2$  ( $F_1$ ,  $m/z$  73) and  $\text{NH}=\text{CH}_2$  ( $F_2$ ,  $m/z$  44 ). It should be noted that in the mass spectra of the amine (6), the peak MI ( $M^+$  103) becomes less noticeable ( $I_{\text{relative}} = 0,3\%$ ). Substitution of the 2-aminoethyl group ( $\text{CH}_2\text{CH}_2\text{NH}_2$ ) in the N- (2-aminoethyl)ethane-1,2-diamine molecule (6) with the  $\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$  group, as expected, radically changes the fragmentation of MI. With increasing the molecular weight and the number of amino groups in diamines, the peak of MI is not observed, that makes it difficult to establish their composition. However, the mass spectra of N, N-Bis(aminoethyl)ethane-1,2-diamine (7) presents characteristic fragment ions with high intensity at  $m/z$  99, 73, 44, which allow to determine molecular weight of the diamine (7) , as well as the direction of MI fragmentation.

The introduction of the phenyl group to the nitrogen atom increases the intensity of the MI peak (8,  $M^+$ -136, Table 1.2) and facilitates the  $\alpha$ -cleavage of the C – C bond between the nitrogen atoms. Such a process leads to a very stable

characteristic fragment ion  $F_1$  at  $m/z$  106 with elimination of  $\text{CH}_2\text{NH}_2$  from MI (Scheme 1).

In the mass spectrum of amine (9) gives a low intense MI peak at  $m/z$  150 (9) and two more intense characteristic peaks at  $m/z$  120 and 91 for the  $[\text{M}-\text{CH}_2\text{NH}_2]^+$  and  $\text{C}_6\text{H}_5\text{C}^+\text{H}_2$  ions, respectively.

Introduction of 3-(trimethoxysilyl)propyl into the ethylenediamine molecule (1) gives a definite effect on nature of the MI fragmentation (10).

The MI peak is absent in mass-spectrum of the compound (10). However, the spectrum gives significant peaks at  $m/z$  192, 130, 121, and 91, as well as a maximum peak at  $m/z$  160 belonging to characteristic ammonium:  $[(\text{H}_3\text{CO})_3\text{Si}-(\text{CH}_2)_3\text{N}^+\text{H}=\text{CH}_2]$  ( $m/z$  192),  $[(\text{H}_3\text{CO})_2\text{Si}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{N}^+\text{H}=\text{CH}_2]$  ( $m/z$  160),  $[\text{H}_3\text{CO}-\text{SiH}=\text{CHCH}_2\text{CH}_2-\text{N}^+\text{H}=\text{CH}_2]$  ( $m/z$  130) and oxonium ions:  $[(\text{H}_3\text{CO})_2\text{Si}=\text{O}^+-\text{CH}_3]$  ( $m/z$  21),  $\text{H}_3\text{C}-\text{SiH}=\text{O}^+-\text{CH}_3$  ( $m/z$  91), which confirm the structure, composition and molecular weight of the compound (10). It should be noted that the positive charge remains on the nitrogen and oxygen atoms in the following sequential processes:  $\text{M}^+ \cdot 222 \rightarrow m/z$  192  $\rightarrow m/z$  160  $\rightarrow m/z$  130 and  $\text{M}^+ \cdot 222 \rightarrow m/z$  121  $\rightarrow m/z$  91.

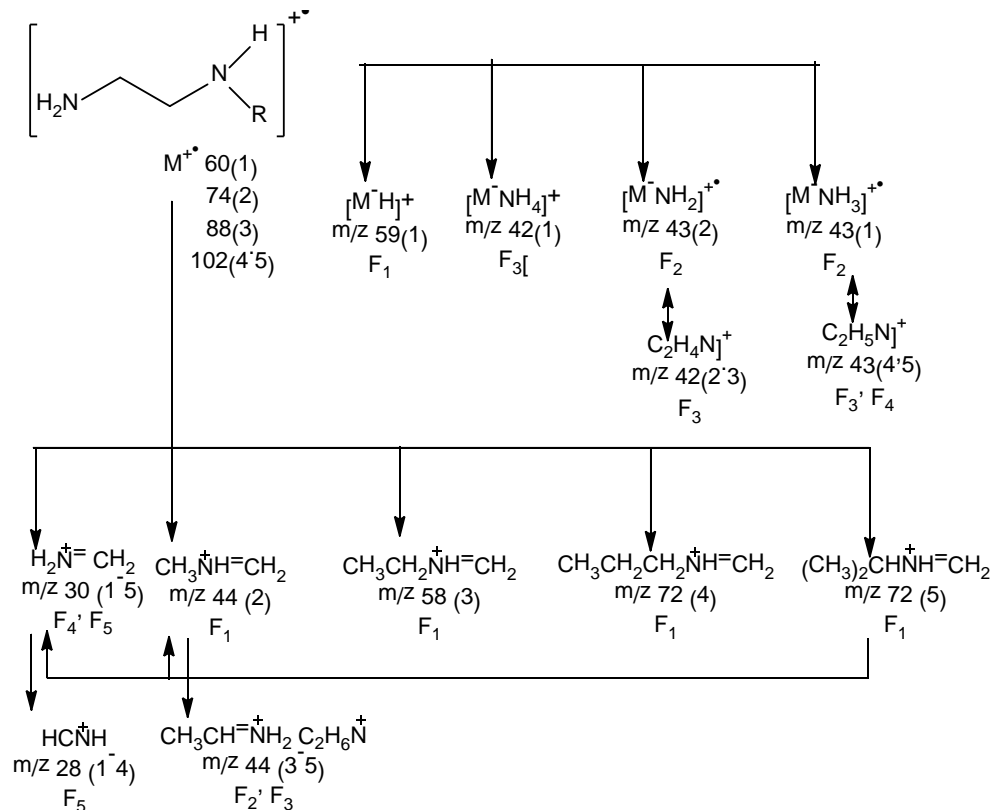
**1,2-Diaminoethane (1).** The mass spectrum gives the MI peak ( $\text{M}^+ \cdot 60$ ) with an intensity of 6.8% (Table 1) and with the stability  $W_{\text{MI}} \approx 3.7$  to EI (Table 2). The spectrum presents a highest peak  $F_4$   $[\text{M}-\text{CH}_2\text{NH}_2]^+$  at  $m/z$  30 ion (Scheme 1), arising from the  $\alpha$ -cleavage of the C – C bond. In addition, the mass spectra of compound (1) gives following significantly intense peaks of ammonium ions:  $\text{NH}_2-\text{CH}_2-\text{CH}=\text{N}^+\text{H}_2$  ( $m/z$  59),  $\text{H}_2\text{C}=\text{CH}-\text{N}^+\text{H}_3$  ( $m/z$  44),  $\text{H}_2\text{C}=\text{C}=\text{N}^+\text{H}_2$  ( $m/z$  42),  $\text{HN}^+\equiv\text{CH}$  ( $m/z$  28) and of cation-radical of etenamine  $[\text{CH}_2=\text{CH}-\text{NH}_2]^+$  at  $m/z$  43 (Scheme 1).

**N-Methylethane-1,2-diamine (2).** The mass spectrum of the amine (2) presents a MI peak ( $\text{M}^+ \cdot 74$ ) at  $m/z$  74 with intensity of 5.4% and stability to IE  $W_{\text{MI}} = 3.0\%$ . The spectrum gives also the maximum peak at  $m/z$  44, arising from the formation of the ammonium cation ( $\text{H}_3\text{C}-\text{N}^+\text{H}=\text{CH}_2$ ) during elimination of the  $\text{CH}_2\text{NH}_2$  group from MI (2) due to  $\alpha$ -cleavage. There are with a resonantly stabilized peak of ammonium ion  $F_1$  at  $m/z$  44, also a noticeable intense peak of the ammonium ion  $F_2$  ( $\text{H}_2\text{C}=\text{N}^+\text{H}_2$ ) at  $m/z$  30 (Scheme 1).

**N-Ethylethanediamine-1,2 (3).** Mass spectrum of diamine (3) is similar to spectrum of the homolog (2), differ only in the intensity of MI, and fragment ions ( $F_1$ ,  $F_2$ ). MI peak ( $\text{M}^+ \cdot 88$ ) has very low intensity ( $I_{\text{om}} = 0.3\%$ ,  $W_{\text{MI}} \approx 1.2$ ; Table 1,2). In contrast to analogue (2), the ammonium characteristic ion  $F_4$  ( $m/z$  30) is formed by an almost equally high probability with  $F_1$  ion at  $m/z$  58 (Scheme 1). This is due to the formation of ammonium ion  $\text{CH}_2=\text{N}^+\text{H}_2$  ( $m/z$  30) from two ions: from MI, arising from  $\alpha$ -cleavage and from the  $F_1$  ion ( $m/z$  58) due to the elimination of the ethyl radical at the nitrogen atom with migration of H- atom to nitrogen and the emission of ethene.

**N-Propylethanediamine-1,2 (4).** Unstable MI ( $\text{M}^+ \cdot 102$ ) by the decomposition reaction leads to three ammonium ions  $F_1$  ( $m/z$  72),  $F_2$  ( $m/z$  44) and  $F_5$  ( $m/z$  30). The peaks of the arising ions ( $F_1$ - $F_5$ ) are most intense (Table 1). The maximum peak among them is like the homologues 2,3 corresponds to the ammonium ion  $F_1$

at  $m/z$  72 ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}^+\text{H}=\text{CH}_2$ ), arising  $\alpha$ -cleavage of the C-C bond between the nitrogen atoms. The processes in  $F_1$  ions with the migration of the H-atom to nitrogen and the emissions of alkenes leads to the  $F_2$  and  $F_5$  ions (Scheme 1).

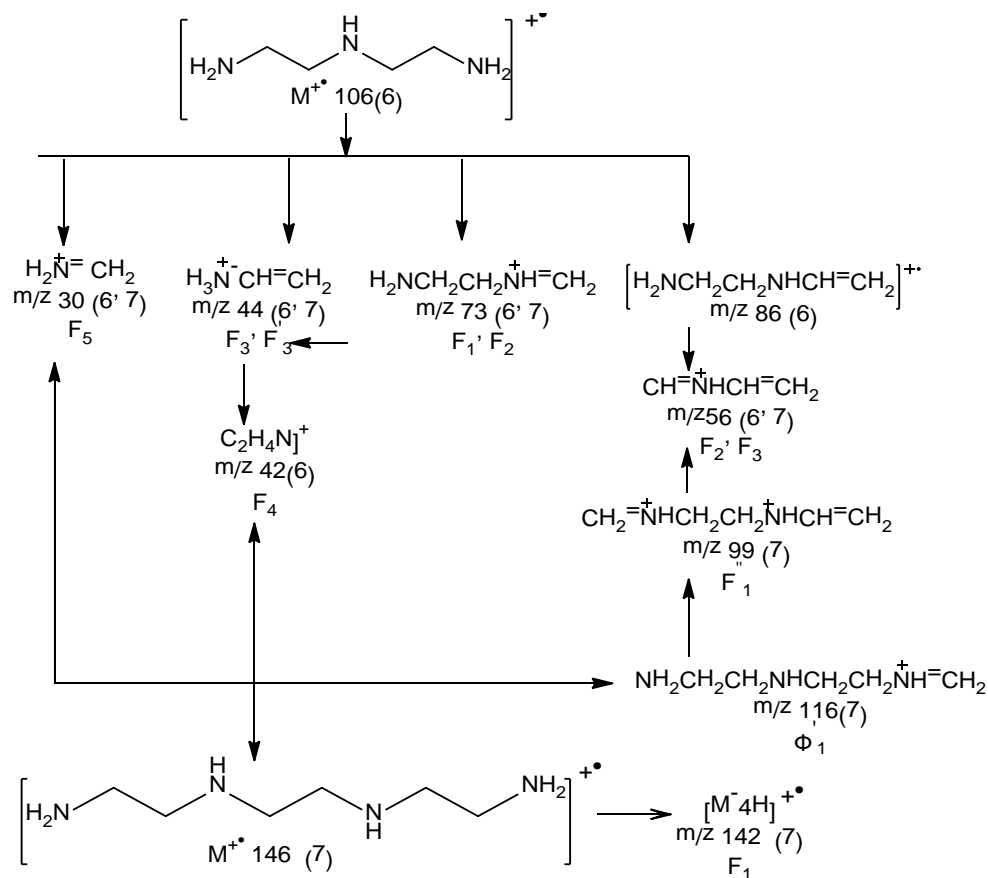


Scheme 1 – The mechanism of MI fragmentation of N-methyl-, ethyl-, propyl-, isopropylethanediamines (2-5) and 1,2-ethanediamine

**N-Isopropylethanediamine-1,2 (5).** The  $\alpha$ -cleavage with the formation of ammonium ions  $(\text{H}_3\text{C})_2\text{CH}-\text{N}^+\text{H}=\text{CH}_2$  at  $m/z$  72 and  $\text{CH}_2=\text{N}^+\text{H}_2$  at  $m/z$  30 destabilizes the MI of N-isopropylethanediamine (5), the peak of which is barely noticeable in MS (Table 1, 2). The MI isomers 4 and 5 are similar by the nature of the decomposition reaction (Scheme 1). However, comparing their mass spectrums shows that the intensity of the characteristic fragment ions  $F_1$ ,  $F_3$  and  $F_5$  at  $m/z$  74, 44 and 30, respectively, is very different (Table 1,2).

**N- (2-Aminoethyl)ethanediamine-1,2 (6).** The introduction of ethylamine groups to the molecule of ethanediamine greatly reduces the intensity of the MI peak and its fragmentation leads to the formation of stable ammonium ions  $F_1$  ( $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^+\text{H}=\text{CH}_2$ ) at  $m/z$  73 and  $F_3$  ( $\text{H}_3\text{C}-\text{N}^+\text{H}=\text{CH}_2$ ) at  $m/z$  44. The formation of these ions is due to the occurrence of two main fragmentation processes, ensuring a high characteristic nature of mass spectrum: the elimination

of the  $\text{CH}_2\text{NH}_2$  at the  $\alpha$ -C-atom between nitrogen atoms; the regrouping process in  $F_1$  ions with the migration of the H-atom and the emission of the  $\text{CH}_2\text{NH}$  (Scheme 2). Mass spectrum of diamine (6) presents significant peaks at  $m/z$ : 86, 56, 30 and 28 (Table 1), due to the ions  $[\text{M}-\text{NH}_3]^+$ ,  $[\text{M}-\text{NH}_3-\text{CH}_2\text{NH}_2]^+$ ,  $\text{H}_2\text{N}^+=\text{CH}_2$  and  $\text{H}_2\text{N}^+\text{C}$ , respectively.



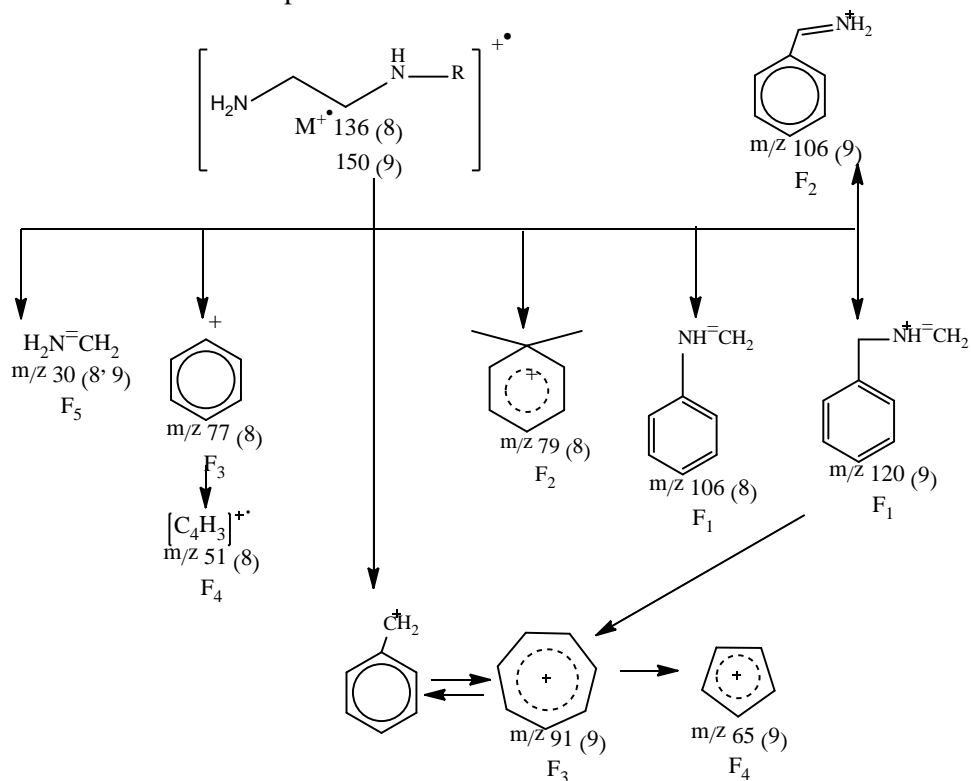
Scheme 2 – The mechanism of MI fragmentation  
of N-(2-aminoethyl)ethanediamine-1,2 (6) and  $N_1,N_2$ -Bis(aminoethyl)ethanediamine-1,2 (7)

**N-(2-Ethylethanediamino)ethanediamine (7).** A somewhat unexpected fragmentation is observed in the case of N-(2-ethylethanediamino)ethanediamine (7). Its mass spectrum practically does not contain a MI peak ( $M^+ 146$ ). However, there are peaks of characteristic fragment peaks:  $[\text{M}-\text{CH}_2\text{NH}_2]^+$  ( $m/z$  116),  $[\text{M}-\text{CH}_2\text{NH}_2-\text{NH}_3]^+$  ( $m/z$  99),  $[\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^+\text{H}=\text{CH}_2]$  ( $m/z$  73) and  $[\text{H}_2\text{N}-\text{CH}_2-\text{CH}_3]^+ \leftrightarrow \text{H}_2\text{N}^+\text{C}$  ( $m/z$  44), confirming the structure and molecular weight of the ethanediamine derivative (7) (Table 1.2, Scheme 2). The formation of a significant  $F_1$  ion ( $m/z$  116) is related to the main process of MI (7) fragmentation – the elimination of  $\text{CH}_2\text{NH}_2$ , similarly to diaminoethane derivatives (1-6). This  $F_1$  ion



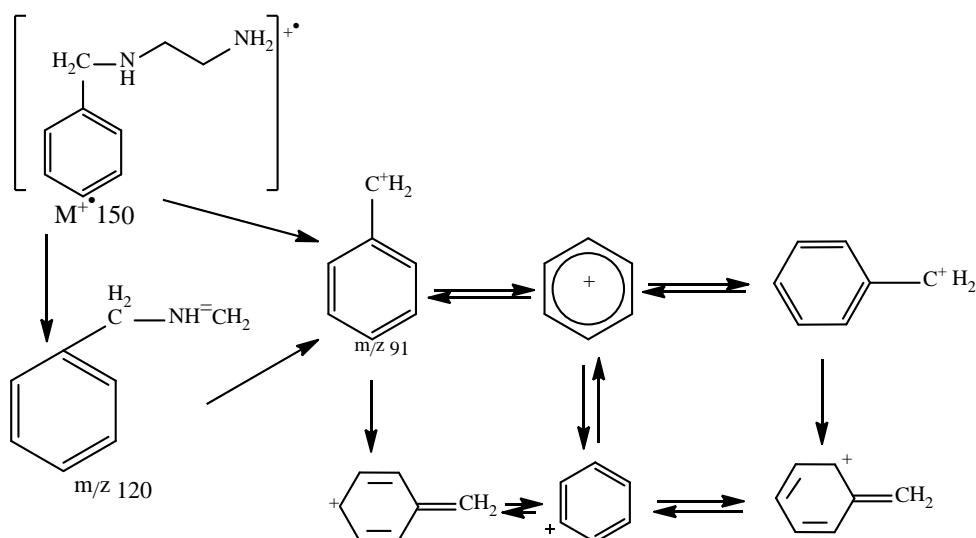
emits  $\text{NH}_2$  molecules by the formation of the  $\text{F}_2$  ion ( $[\text{CH}_2=\text{N}^+\text{H}-\text{CH}_2\text{CH}_2\text{NH}-\text{CH}=\text{CH}_2]$ ) at  $m/z$  99 with an intensity of peak -20% (Table 1.2). An intense peak at  $m/z$  73 ( $I_{\text{relative}}=41\%$ ) corresponds to the  $\text{F}_3$  ion by splitting of the molecule (7). In the mass spectrum a maximum peak of the ammonium ion  $\text{F}_4$  ( $I_{\text{relative}}=100\%$ ), the formation of which probably carries out from MI (7) from the primary, secondary ammonium ions ( $\text{F}_1$ - $\text{F}_3$ ). It should be noted that the noticeable MI peak ion at  $m/z$  142 is due to the emission of two  $\text{H}_2$  molecules from MI (7).

**N-Phenylethanediamine-1,2 (8).** The introduction of phenyl group into the ethanediamine molecule (1) increases the stability of MI (8) to EI (Table 1.2) and its intensity in mass spectrum reaches  $I_{\text{relative}}=15\%$  (Table 1). The most maximum peak of ammonium ion  $\text{C}_6\text{H}_5\text{-N}^+\text{H}=\text{CH}_2$  ( $\text{F}_1$ ) at  $m/z$  106 is formed as a result of  $\alpha$ -cleavage of C-C bond, and also significant ammonium ion  $\text{CH}_2=\text{N}^+\text{H}_2$  ( $\text{F}_5$ ) at  $m/z$  30, due to charge localization on the N atom of the unsubstituted part of ethanediamine (Scheme 3). The fragment  $\text{F}_1$  ion loses  $\text{HCN}$  molecule as a result of the secondary regrouping process ( $\text{F}_2$ , with  $m/z$  79). The mass spectrum (8) presents an intense peak of the phenyl cation ( $\text{F}_3$ ) at  $m/z$  77, as well as significant peaks of "aromatic series" ions  $[\text{C}_5\text{H}_5]^+$ ,  $[\text{C}_4\text{H}_3]^+$  and  $[\text{C}_3\text{H}_3]^+$  at  $m/z$  65, 51, 39 that indicates the presence of a phenyl substitution in the molecule. The mechanism of formation of characteristic ions is presented in Scheme 3.



Scheme 3 – The mechanism of MI fragmentation of N-Phenylethanediamine-1,2 (8) and N-Benzylethanediamine-1,2 (9)

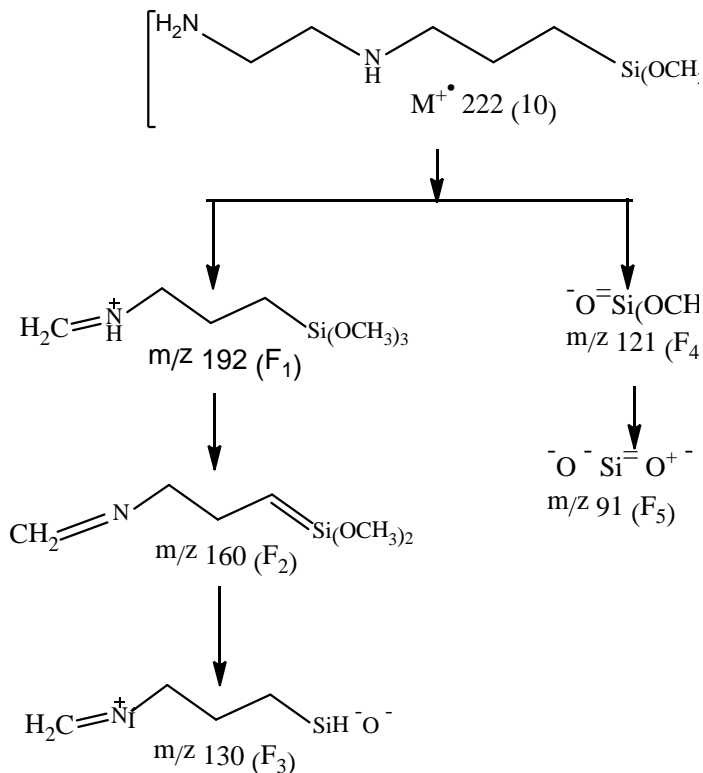
**N-Benzylethanediamine (9).** As in the case of N-phenylethanediamine (8), the main directions of fragmentation of N-benzylethanediamine-1,2 (9) are initiated by unpaired electrons of the nitrogen atom. All the most intense peaks in mass spectrum of compound (9) are due to ions formed as a result of primary  $\alpha$ -cleavage or secondary regrouping, because the nitrogen atom has a high tendency to retain charge. However, the replacement of the phenyl radical in the molecule of N-phenylethanediamine (8) with a benzyl destabilizes the stability of MI to EI and significantly changes the picture of mass spectrum of diamine (9). For this compound (9), the benzyl cleavage becomes the dominant fragmentation process with the formation of a resonantly stabilized benzyl or tropylium cation by the next mechanism:



Thus, the main fragmentation process of unstable MI ( $M^+ \cdot 150$ ) is associated with the successive elimination of  $\text{CH}_2\text{NH}_2$  ( $F_1$ , with  $m/z$  120) and  $\text{NH}=\text{CH}_2$  ( $F_3$ , with  $m/z$  91) radicals with the formation of a resonantly stabilized tropylium cation (Table 1.2, Scheme 3).

**N-[3-(Trimethoxysilyl)propyl]ethanediamine-1,2 (10).** There is no MI peak ( $M^+ \cdot 222$ ) in mass spectrum of the compound (10) (Table 1,2). However, mass spectrum gives an intense peak of the characteristic ammonium ions  $F_1$  at  $m/z$  192, arising from  $\alpha$ -cleavage of the C – C bond between nitrogen atoms (cleavage of the  $\text{CH}_2\text{NH}_2$  radical). The mass spectrum presents a more intense peak of the stable ammonium ion  $F_2$  at  $m/z$  160, which confirm structure and molecular weight of the compound (10). Scheme 4 shows the main directions of MI fragmentation (120) and the basic processes characteristic of the decomposition reaction of the molecule of diamine (10). In MS the most intense peaks of characteristic ions  $F_1$  ( $m/z$  192),  $F_2$  ( $m/z$  160) and  $F_3$  ( $m/z$  130) are observed, which are connected by successive processes of elimination of particles:  $\text{CH}_2\text{NH}_2$ ,  $\text{CH}_3\text{OH}$  and  $\text{CH}_2\text{O}$  from MI (10). It

is shown that the  $\text{CH}_2\text{NH}_2$  radical is ejected in the same way as ethanediamines (1–9), then the  $\text{CH}_3\text{OH}$  molecule (F2) are eliminated from this  $\text{F}_1$  ion, then the most stable ammonium ion  $\text{F}_2$  emits a molecule of  $\text{CH}_2\text{O}$  due to the regrouping and migration of the H atom with the formation of the third ammonium ion  $\text{F}_3$  (Scheme 4).



Scheme 4 – The mechanism of MI fragmentation of N- [3- (trimethoxysilyl)propyl]ethanediamine-1,2 (10)

The MS of diamine (10) presents the significant peaks at  $m/z$  121, 91, 44, 32, 31, corresponding to oxonium ions  $\text{F}_4$  ( $m/z$  121),  $\text{F}_5$  ( $m/z$  91) and ammonium ion  $\text{F}_6$   $\text{CH}_3\text{N}^+\text{H}=\text{CH}_2$  ( $m/z$  44) and  $[\text{H}_3\text{C}-\text{OH}]^+$  ( $m/z$  32) ions,  $[\text{H}_2\text{C}=\text{O}^+\text{H}]$  ( $m/z$  31).

Thus, the cleavage of the radical  $\text{CH}_2\text{NH}_2\text{C}$  is characterized with the formation of a stable ammonium ion for the considered monosubstituted derivatives of 1,2-diaminoethan. The stability of MI to EI is very low, with the exception of N-phenylethanediamine-1,2. The main processes of MI fragmentation are associated with the formation of stable characteristic ammonium ions, which allow them to successfully carry out mass spectrometric interpretation.

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## Резюме

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1,2-ДИАМИНЭТАННИҢ КЕЙБІР БІРОРЫНБАСҚАН  
ТУЫНДЫЛАРЫНЫҢ МАСС-СПЕКТРЛЕРІ

Этандиаминнің он бірорынбасқан туындыларының масс-спектрлері қарастырылып, олардың салыстырмалы сараптамасы жүргізілген. Олардың молекулалық иондарының фрагментация ерекшеліктері сипатталған және көрсетілген. Молекулалық иондардың ыдырау реакциясының бағыты орынбасарлардың табиғатына тәуелділігі анықталған. Электронмен ионизациялау жағдайда ең маңызды болып  $\alpha$ -бөлініуі және оң заряд N атомында шоғырланатыны және осы процестер әсерінде тұрақты аммоний иондарының пайда болатыны анықталған және көрсетілген.

**Түйін сөзер:** 1,2-диаминоэтан, масс-спектр, аммоний иондар, молекулалық ион, электрондармен ионизациялау.

## Резюме

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МАСС-СПЕКТРЫ НЕКОТОРЫХ МОНОЗАМЕЩЕННЫХ  
ПРОИЗВОДНЫХ 1,2-ДИАМИНОЭТАНА

Рассмотрены масс-спектры монозамещенных производных 1,2-диаминоэтана и проведен их сравнительный анализ. Показаны и обсуждены особенности фрагментации молекулярных ионов производных 1,2-диаминоэтана. Установлено, что направление реакции распада молекулярных ионов зависит от природы заместителей. Выявлено, что в условиях ионизации электронами наиболее важным является  $\alpha$ -разрыв с локализацией положительного заряда на атоме азота, который приводит к образованию устойчивых аммониевых ионов.

**Ключевые слова:** 1,2-диаминоэтан, масс-спектр, ионы аммония, молекулярный ион, электронная ионизация.