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Positive Charge Distribution of Secondary Alkylamines and Its Correlation with the Bond-Scission Probability Appearing in Their Mass Spectra[1]

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With respect to the correlation between scission probabilities and positive charge distributions on the skeletal bonds of amines appearing in their mass spectra, further research is reported on four secondary amines (diethylamine, dipropylamine, dibutylamine and methylbutylamine). In each secondary alkylamine the fragment ions formed by the scission of α–CC bond are the most abundant experimentally, *i. e.*, the scission probability of α–CC bond is the largest in monoamines as well. Agreement between experiments and LCBO-MO calculations on four secondary alkylamines is found to be satisfactory as in the case of propylamine, using the same semi-empirical parameters as those of monoamines in the calculation. It is shown that from detailed calculations of diethylamine by CNDO method the scission of α–CC bond is also easy due to concentration of the positive charge at the bond, theoretically in accordance with the semi-empirical calculation. Change of mass spectra *vs.* ionizing voltage is explained on a generalized scheme, which combines two existing theories of fragmentation (QET and MOT).

We have shown that the molecular orbital theory (MOT) for mass spectra can explain quantitatively the skeletal fragmentation of compounds such as normal[4] and cyclic alkanes,[5] ketones,[6] amines,[7] ethers,[8] esters[9] and aminoacid esters.[10] In MOT it is assumed that relative scission probability of each skeletal bond of of the electron-bombarded molecule is proportional to the positive charge distribution of the highest occupied molecular orbital (HO–MO) at the corresponding bond of its molecular ion, where the positive charge distribution means the distribution of the positive hole formed by losing an electron from the HO–MO of the neutral molecule. Thereby, knowledge of the con-

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stants characteristic to each functional group is required for calculation of the HO–MO, except for normal and cyclic alkanes.

As far as the mass spectra of the normal and cyclic alkanes are concerned, the above assumption seems to be acceptable.[11] Several comments have been given on the use of the assumption for predicting the mass spectra of the compounds containing heteroatoms. Lorquet et al.[12] criticized the use of calculated results of alkylamines based on the LCBO–MO approximation in our attempt to extend the research to normal alkylamines, *i. e.*, although the positive charge densities at the CN bond and lone pair are 16% and 71% of the total, respectively, only that at the CC bond is taken in discussing the scission probability. In the LCBO–MO approximation, however, the positive charge distribution of the lone pair is included implicitly in that of the CN bond, so that net charge distribution at the CN bond might occupy only a small fraction of the total and be even smaller than that of the α–CC bond adjacent to it. We therefore adopted in our previous work on ethylamine and propylamine[13] the CNDO (the complete neglect of differential overlap) method of LCAO–MO–SCF proposed by Pople *et al.*[14] The results were found to be favorable.

In our research[6] on propyl-, butyl-, amyl-, hexyl- and heptylamine, calculation was carried out by the LCBO–MO method, and two parameters concerned with amino group were determined empirically from the observed values of propylamine and butylamine. The parameters were found transferable also in the calculation of alkyldiamines from C_4 to C_7[7b] and aminoacid esters.[10]

We report herewith that a good agreement can be found for four secondary alkylamines between the calculated values obtained by the LCBO–MO method and the observed from mass spectra by use of the two parameters of the primary amines, and also diethylamine by use of the calculated positive charge obtained by the CNDO method.

Calculations

LCBO-MO Method. According to the assumption, the scission probability of the skeletal bonds is proportional to the positive charge densities of the HO–MO of the molecular ion. In actual calculation, the charge densities are assumed to be equal to the electron densities of the corresponding neutral molecule, calculated by the LCBO–MO method. The MO belonging to the skeletal bond Φ is given by

$$\Phi = \sum_{i=1}^{n} c_i \phi_i, \qquad (1)$$

where ϕ_i is the bond-orbital of the i-th skeletal bond. The summation is carried out on all the bond adopting the united atom approximation.[15]

The secular equation of a molecule is

$$|e_{ij} - \delta_{ij}E| = 0, \qquad (2)$$

where e_{ij} denotes the matrix element and E the energy of the molecular orbital. All the interactions except for those adjacent group bonds are assumed to be zero. The required parameters in the calculation are the Coulomb integrals of CN and α-CC bond and resonance integral of CN bond as follows.

$$\alpha_{C-N} = \alpha_0 + 0.5\beta_0,\ \alpha_{C-CN} = \alpha_0 - 2.0\beta_0,\ \beta_{C-N} = \beta_0 \qquad (3)$$

where α_0 and β_0 are the Coulomb integral and the resonance integral of normal alkane, respectively. The parameters in Eq. (3) were determined from the experimental values of propylamine and butylamine.[7a]

CNDO Method. The CNDO method is a semi-empirical LCAO–MO–SCF method calculating molecular orbitals and is known to be applicable to π electrons and lone pair electrons as well as σ electrons. Nine possible conformations of diethylamine and three of methylethylamine were calculated. Atomic distances of both amines were adopted as follows: C–C, 1.540 Å; C–N, 1.474Å; C–H, 1.085Å; N–H, 1.012Å.

Table 1. Matrix elements $U_{\mu\mu}$ (in electron volts)

	H	C	N
s orbital	−7.176	−14.051	−19.316
p orbital	—	−5.572	−7.275

$U_{\mu\mu} = (\mu|-\frac{1}{2}\nabla^2 - Z_A/r_{1A}|\mu)$

All the bond angles were taken to be 109°28′. Atomic integrals necessary in the calculation were the same as in the paper of Pople and Segal[14] (Table 1). In the calculation of electron densities, $2s$, $2p_x$, $2p_y$, $2p_z$, orbitals of nitrogen and carbon atoms were adopted as the basis set of orbitals, which were transformed into sp^3-hybrid orbitals after the calculation.

Experimental

The mass spectra were measured on a high resolution type apparatus (Hitachi RMU-7HR), its resolution being *ca.* 5000, and on an ordinary one (Hitachi RMU-5B) installed at Osaka University. Ionization voltage (V_i) was varied in several steps from 10 to 80 volts, the repeller voltage being fixed at 3 volts. The gas-reservoir temperature was maintained at about the boiling point of each sample during the course of measurement. The compounds studied were diethylamine, dipropylamine, dibutylamine and methylbutylamine.

Results

Mass Spectra of Secondary Amines. The mass spectra of four secondary amines at V_i=80 and 20 volts and abundance ratios of the ions in the main peaks from the high resolution measurement are shown in Tables 2 and 3, respectively.

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TABLE 2. MASS SPECTRA OF *sec*-AMINES

m/e	$(C_2H_5)_2NH$		$(C_3H_7)_2NH$		$(C_4H_9)_2NH$		$CH_3NHC_4H_9$	
	80V	20V	80V	20V	80V	20V	80V	20V
15	1.9		6.8		5.2		5.2	
27	10.5		27.0	1.4	25.8		10.8	
28	13.5	1.8	19.6	1.8	18.9	0.3	12.7	
29	11.5	4.7	11.2	0.5	33.9	2.9	8.2	1.1
30	59.5	45.7	85.7	57.4	58.5	31.7	12.3	6.4
39			11.8		11.7		5.1	
41	3.2		21.1	4.1	24.0	4.3	6.7	1.1
42	8.5	1.8	9.0	1.2	8.2	0.7	6.6	0.9
43	2.5	0.2	31.7	13.2	10.8	1.6	4.8	1.4
44	27.1	18.4	14.0	12.6	65.6	60.9	100.0	100.0
56	3.2	1.3	4.0	0.8	6.4	0.9	2.6	0.7
57	0.9	0.2	0.5	0.2	17.5	7.3	3.2	1.4
58	100.0	100.0	6.2	4.5	1.6	0.9	7.1	5.9
70			3.4	1.2	1.8	0.4	0.9	0.3
72	16.7	16.7	100.0	100.0	6.9	5.9	2.9	2.4
73	31.1[a]	33.9	5.0	5.0				
84					1.7	0.9		
86			0.3	0.3	100.0	100.0	8.1	7.7
87					5.9	6.0	8.4	10.9
100			2.2	2.1	0.6	0.6		
101			13.8	14.8				
128					1.6	1.4		
129					12.1	13.9		

a) Underlined values denote parent peaks.

TABLE 3. THE ABUNDANCE RATIOS OF IONS BY HIGH RESOLUTION MEASUREMENT (%)

m/e	Ion	$(C_2H_5)_2NH$		$(C_3H_7)_2NH$		$(C_4H_9)_2NH$		$CH_3NHC_4H_9$	
		80V	20V	80V	20V	80V	20V	80V	20V
27	$(CNH)^+$	3		2	11	2	37	6	46
	$(C_2H_3)^+$	97		98	89	98	63	94	54
28	$(CNH_3)^+$	90	91	89	66	82	53	87	72
	$(C_2H_4)^+$	10	9	11	34	18	47	13	28
29	$(CNH_3)^+$	11	6	37	21	10	2	19	8
	$(C_2H_5)^+$	89	94	63	79	90	98	81	92
41	$(C_2NH_3)^+$			7		7		27	12
	$(C_3H_5)^+$			93	100	93	100	73	88
42	$(C_2NH_4)^+$			79	69	100	100	100	100
	$(C_3H_6)^+$			21	31				
43	$(C_2NH_5)^+$			17	4	81	78	86	86
	$(C_3H_7)^+$			83	96	19	22	14	14

The largest peak of each amine arose from the ion formed by the scission of α-CC bond as in primary amines, *i. e.*, diethylamine, *m/e* 58 $(C_2H_5NHCH_2)^+$; dipropylamine, *m/e* 72 $(C_3H_7NHCH_2)^+$; dibutylamine, *m/e* 86 $(C_4H_9NHCH_2)^+$; methylbutylamine, *m/e* 44 $(CH_3NHCH_2)^+$.

From the high resolution mass spectra (Table 3), ions of *m/e* 43 of dipropylamine are found to consist of $(C_2NH_5)^+$ (20%) and $(C_3H_7)^+$ (80%), while in dibutylamine and methylbutylamine the ratios of both ions in *m/e* 43 are the reverse. The differences are caused by the processes giving $(C_3H_7)^+$ such that scission at the CN bond occurs in dipropylamine while at the α-CC bond in the latter two amines.

The peaks derived from the metastable ions and the fragmentation processes are shown in Table 4. The metastable peaks were fairly large (Fig. 1). In primary amines they could not be observed. We see from Table 4 that the ions of *m/e* 30 and *m/e* 44 are assigned to be those formed by secondary scission (except for *m/e* 44 of methylbutylamine). In the case of dipropylamine, after the ion of *m/e* 72 was first formed by the

Table 4. Meta-stable peaks of *sec*-amines and their fragmentation processes

Amine	Fragmentation process	Obsd. m^*	Calcd. m^*
$(C_2H_5)_2NH$	$(CH_2NHC_2H_5)^+$ m/e 58 → $(CNH_4)^+$ m/e 30	15.5	15.5_2
	?	22.8	
$(C_3H_7)_2NH$	$(CH_2NHC_3H_7)^+$ m/e 72 → $(CNH_4)^+$ m/e 30	12.5	12.5_0
	$(CH_2NHC_3H_7)^+$ m/e 72 → $(C_2NH_6)^+$ m/e 44	26.9	26.8_8
$(C_4H_9)_2NH$	$(CH_2NHC_4H_9)^+$ m/e 86 → $(CNH_4)^+$ m/e 30	10.5	10.4_6
	$(NHC_4H_9)^+$ m/e 72 → $(CNH_4)^+$ m/e 30	12.5	12.5_0
	$(CH_2NHC_4H_9)^+$ m/e 86 → $(C_2NH_6)^+$ m/e 44	22.5	22.5_1
$CH_3NHC_4H_9$	$(NHC_4H_9)^+$ m/e 72 → $(CNH_4)^+$ m/e 30	12.5	12.5_0
	$(CH_3NHC_4H_9)^+$ m/e 87 → $(C_2NH_6)^+$ m/e 44	22.3	22.2_5

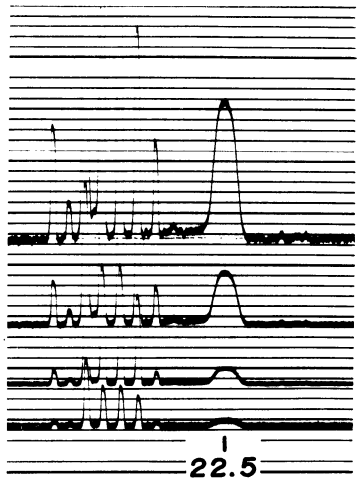

Fig. 1. Metastable peak of dibutylamine.

scission of α-CC bond, the scission at the residual α-CC bond produced the m/e 44 and the successive scission at CN bond produced the m/e 30. Both ions were the rearrangement ions. They did not decrease practically by lowering the ionizing voltage. Thus the phenomenon differs from the case of primary amines.

Scission Probabilities. The observed scission probabilities were evaluated by using ordinary mass spectra and the individual high resolution mass spectra for the necessary ions. As an example, in the case of dipropylamine, it was considered that since the ions of m/e 30 and m/e 44 were formed by the secondary scission of the m/e 72, the ion formed by the scission at the α-CC bond was the sum of the ions of m/e 72, m/e 30 and m/e 44. In the case of methylbutylamine, it was also possible that the ion of m/e 30 was formed by the scission at the CN bond of butyl group. The m/e 30 ion through process A is produced by the primary scission at the CN bond of butyl group (Bond 1) and that through process B is produced by the secondary scission of m/e 72 ion (Bond 1′ and 2).

$$CH_3\overset{1'}{-}NH\overset{1}{-}CH_2\overset{2}{-}CH_2\overset{3}{-}CH_2\overset{4}{-}CH_3$$

$\nearrow$ $(CNH_4)^+$ m/e 30 (A)

$\searrow$ $(NHCH_2CH_2CH_3)^+$ m/e 72 → $(CNH_4)^+$ m/e 30 (B)

Since the origin of these ions cannot be distinguished experimentally yet, the amount of the ion through process A and that through process B were estimated to be half, assuming that these two processes were brought about in a simillar proportion. The observed values thus estimated are shown in Table 5 in comparison with those calculated by the LCBO–MO method.

Table 5. Scission probabilies of the skeletal bonds (%)

Amine		Bond Number[a] 1	2	3	4(4+1′)
$(C_2H_5)_2NH$	Exp. 80V	26.7	73.3		
	20V	14.3	85.7		
	Calcd.	20.0	80.0		
$(C_3H_7)_2NH$	Exp. 80V	14.7	83.5	1.8	
	20V	10.7	89.1	0.2	
	Calcd.	14.4	74.9	9.7	
$(C_4H_9)_2NH$	Exp. 80V	18.9	65.1	14.6	1.4
	20V	13.9	84.3	1.8	0.0
	Calcd.	13.5	73.2	11.9	1.5
$CH_3NHC_4H_9$	Exp. 80V	14.6	64.9	15.4	5.1
	20V	5.7	84.8	7.3	2.2
	Calcd.	8.7	75.6	13.2	2.6

a) Bond Number

$$C\overset{3}{-}C\overset{2}{-}C\overset{1}{-}N\overset{1}{-}C\overset{2}{-}C\overset{3}{-}C$$
$$C\overset{1'}{-}N\overset{1}{-}C\overset{2}{-}C\overset{3}{-}C\overset{4}{-}C$$

The calculated values by the CNDO method are given in Table 6. The subscripts for each carbon atom are the same as those in Fig. 2. The positive charge distributions of the HO–MO of each conformation are shown in %, where the mean value was evaluated on the assumption that the contribution was equal. About 40% of the positive charge is located at the lone pair orbitals. From the table, the positive charge distributions of the HO–MO at the skeletal bonds were calculated by summing up those of the atomic orbitals which constituted the skeletal bonds and normalizing these values. The positive charge distributions concerned with the skeletal bonds are indicated in Fig. 3. The positive charge distribution of the α-CC bond contains about 60% of the total charge, and the expected tendency of easy scission at the α-CC bond is realized experimentally.

TABLE 6. CHARGE DISTRIBUTION OF THE HO ORBITALS OF DIETHYLAMINE

Atomic Orbitals			C-N *trans*			C-N *gauche* I			C-N *gauche* II			Mean value
Numbering		Relating bond	I	II	III	I	II	III	I	II	III	
N	1	Lone pair	53.9	53.2	53.5	53.5	53.3	0.0	53.2	53.3	0.0	41.5
	2	CN (I)	0.9	1.1	0.9	1.1	1.2	1.2	0.7	0.8	1.2	1.0
	3	CN (II)	0.9	0.7	1.1	0.9	0.8	1.0	1.1	1.2	1.2	1.0
	4	NH	0.9	1.0	0.8	0.8	0.9	0.0	1.0	0.9	0.0	0.7
C_I	5	CN	1.7	1.9	1.7	2.1	2.1	0.5	1.4	1.6	0.5	1.5
	6	α-CC	0.4	0.7	4.4	0.4	0.6	0.1	0.5	4.4	0.1	1.3
	7	CH	3.4	0.2	0.7	3.6	0.2	1.0	0.5	0.7	1.0	1.3
	8	CH	0.4	3.4	0.2	0.3	3.6	0.2	3.4	0.3	0.1	1.3
C_{II}	9	α-CC	0.9	1.6	8.2	0.9	1.4	0.2	1.0	8.3	0.1	2.5
	10	CH	0.0	0.1	0.4	0.4	0.5	22.5	0.0	0.0	22.5	5.2
	11	CH	0.0	0.0	0.8	0.1	0.0	0.7	0.4	0.6	0.8	0.4
	12	CH	0.4	0.6	0.0	0.0	0.1	0.0	0.0	0.4	0.1	0.2
C_{III}	13	CN	1.7	1.4	2.1	1.7	1.6	0.6	1.9	2.1	0.5	1.5
	14	α-CC	0.4	0.5	0.4	4.4	4.4	0.1	0.7	0.6	0.1	1.3
	15	CH	3.4	3.4	3.6	0.2	0.3	1.0	0.2	0.2	1.0	1.5
	16	CH	0.4	0.5	0.3	0.7	0.7	1.0	3.4	3.6	0.1	1.1
C_{IV}	17	α-CC	0.9	1.0	0.9	8.2	8.3	0.1	1.6	1.4	0.1	2.5
	18	CH	0.0	0.0	0.1	0.4	0.4	0.8	0.1	0.1	0.8	0.3
	19	CH	0.0	0.0	0.0	0.8	0.7	22.2	0.5	0.5	22.5	5.2
	20	CH	0.4	0.4	0.4	0.0	0.0	0.1	0.0	0.0	0.1	0.2
H	21	CH	0.1	0.3	0.5	1.2	1.3	15.4	0.1	0.0	15.6	3.8
	22	CH	0.1	0.0	0.6	0.2	0.0	3.3	1.1	0.5	0.1	0.7
	23	CH	1.2	1.4	0.0	0.2	0.0	0.1	0.1	0.8	3.4	0.8
	24	CH	9.7	0.8	1.7	9·9	0.9	4.1	1.7	1.7	3.9	3.8
	25	CH	1.6	9.6	0.6	1.5	9.8	1.0	9.8	0.8	0.6	3.9
	26	NH	3.1	3.3	2.8	2.8	3.0	0.0	0.3	3.0	0.0	2.0
	27	CH	9.7	9.8	9.9	0.6	0.8	0.6	0.8	0.9	3.9	4.1
	28	CH	1.6	1.7	1.5	1.7	1.7	3.8	9.6	9.8	0.6	3.6
	29	CH	0.1	0.1	0.2	0.8	0.8	3.4	0.3	0.2	3.4	1.0
	30	CH	0.1	0.1	0.1	0.6	0.5	15.6	1.4	1.3	0.1	2.2
	31	CH	1.2	1.1	1.2	0.0	0.0	0.1	0.0	0.0	15.6	2.1

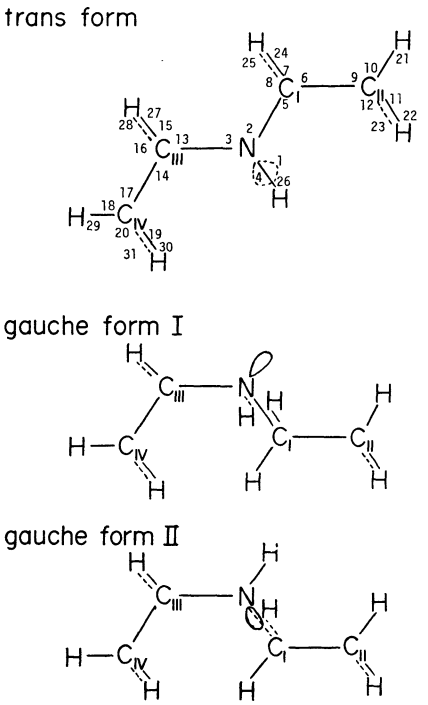

Fig. 2. Numbering of atomic orbitals of diethylamine used in CNDO-calculation.

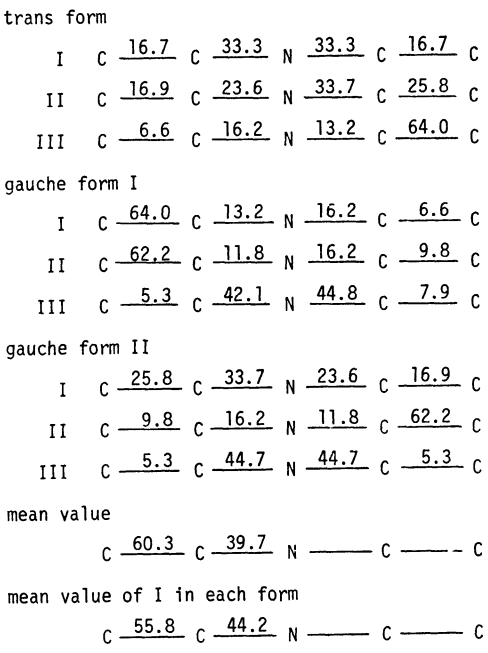

Fig. 3. Positive charge distribution of the HO orbital on the skeletal bond (%).

Discussion

The Quasi-Equilibrium Theory (QET)[16] and the molecular orbital theory (MOT) for mass spectra deal with an explanation of the production processes of the ions appearing in mass spectra. According to QET, the ions are produced by the thermal unimolecular decomposition of molecular ions in high vibrational excited states by the electron bombardment. According to MOT, they are produced by the autoionization from molecules in the superexcited states by the electron bombardment. As shown by the investigations of Platzman[17] and Hatano *et al.*[18], the ion production from the superexcited state is predominant at the bombarding voltage V_i higher by several volts or above than the ionization potential, while the radical production from the superexcited state is predominant at V_i near the ionization potential. Thus, at lower V_i the ions are produced mostly by the unimolecular decomposition explaned by QET, but at higher V_i they are produced *via* the superexcited state explained by MOT in addition to that by QET.

A comparison of the 30V and 80V-mass spectra shows that the fraction of fragment ion peaks losing many hydrogen atoms such as $(C_2H_3)^+$ and $(C_3H_3)^+$ is large in the 80V-mass spectrum, but there is little in the main peaks of both spectra. From the comparison of 30V and 80V-mass spectra, it is indicated that bombarded molecules absorb energy of about 30 eV, while the difference between 20V and 80V-mass spectra is very large as shown in Table 2, the mass spectra changing markedly for making 30eV the border. This is in line with the result in radiation chemistry whose mean total energy accepted by the molecules bombarded with high energy radiation is about 30 eV. As V_i approaches the ionization potential, the selective scission of the bonds obeying the scheme of QET becomes more predominant, making that of MOT less on the contrary. At higher V_i the scission obeying the schemes of MOT and QET takes place simultaneously, but it might be explained mainly by MOT, its interpretation agreeing with the mass spectra of amines. It can thus be concluded that at V_i near the ionization potential most of the ions are produced by the scheme of QET; the higher V_i, the larger the contribution of the scheme of MOT to production of the ions.

The scission probability calculated by the LCBO–MO method and the experimental results (V_i=80V and 20V) in Table 5 are compared in Fig. 4. The parameters used in the calculation by LCBO–MO method were determined empirically from the mass spectra of propylamine and butylamine. Agreement between calculation and experiment is satisfactory. These findings indicate that the parameters can be transferred to secondary amines. Their transferability is also given in the explanation of aminoacid esters.[10] The present results of diethylamine obtained by the

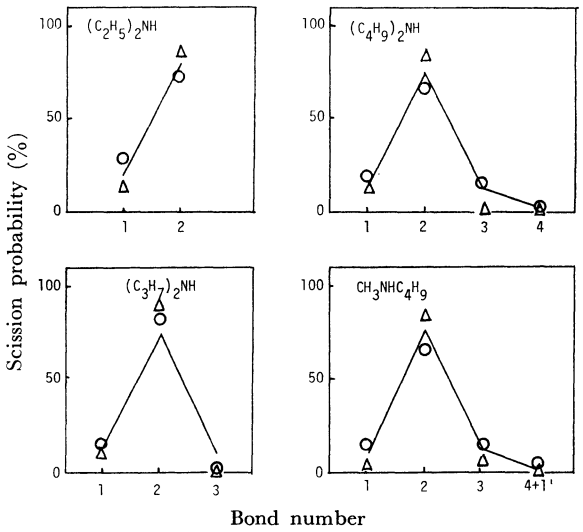

Fig. 4. Scission probability of the skeletal bonds of secondary amines.
○: V_i=80 V., △: V_i=20 V., —: Calcd.

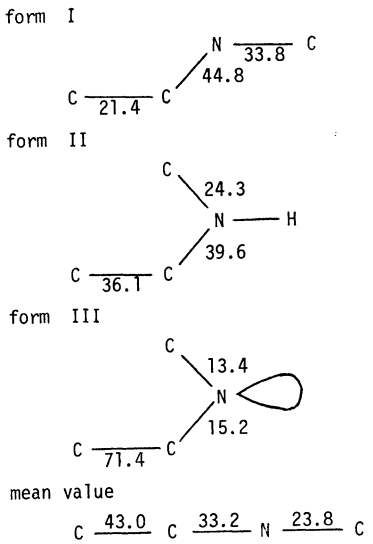

Fig. 5. Positive charge distribution of the HO orbital on the skeletal bond (%).

calculation of the CNDO method offers a good support to the semi-empirical result. Moreover, in the CNDO-calculation of methylethylamine their mean charge density concerning the skeletal bonds is the largest at the α-CC bond (Fig. 5).

Agreement between calculation and experiment is better at higher V_i than at lower V_i in the cases of secondary amines, and the degree of agreement is superior to the case of propylamine. The fragment ions produced by QET and by MOT are observed simultaneouly in mass spectra. The alkanes produce many fragment ions at higher V_i, especially the ions of small carbon numbers such as $(C_2H_4)^+$, $(C_2H_5)^+$, $(C_3H_5)^+$, $(C_3H_7)^+$ which occupy most of the fragment ions. They might be considered to be secondary fragment ions produced by QET. On the other hand, changes of mass spectra against the variation of bombarded voltages are relatively small in these amines. This

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17) R. L. Platzman, *Voltex*, **23**, 372 (1962).
18) Y. Hatano, S. Shida, and S. Sato, This Bulletin, **41**, 1120 (1968); Y. Hatano, *ibid.*, **41**, 1126 (1968).

suggests that the secondary scission originating successively from the first scission might be very few.

With respect to the production of fragment ions of lower hydrocarbons at the skeletal scission, Stevenson concluded that the fragment with the higher carbon number of the two fragments produced from the molecular ion becomes an ion, while the other becomes a radical.[19] Saito et al.[20] indicated that good correlations existed between the amount of the fragmentions and the positive charge in them for the higher hydrocarbons. Most of the peaks appearing in the mass spectra of amines are originated from the ions containing N-atoms such as *m/e* 30 $(CNH_4)^+$, *m/e* 44 $(C_2NH_6)^+$, *m/e* 86 $(C_3NH_{12})^+$. Positive charges of each group containing those of CH bond, NH bond and lone pair obtained by CNDO-calculations, are given in Fig. 6. When the α-CC bond is broken the

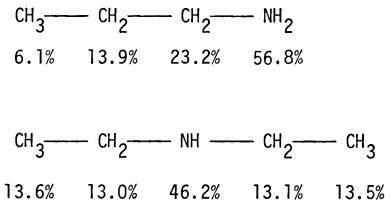

Fig. 6. Charge density of each group calculated by CNDO method.

positive charge of the fragments containing N-atom occupies 80% in propylamine and 87% in diethylamine. From the experimental results total amount of the fragment ions containing N-atom formed by the scission of α-CC bond occupies 92% in propylamine and 99% in diethylamine. Though the correlation of positive charge *vs.* amount of ions with amines is not so good as with hydrocarbons, it is suggested that the fragment having more charge of the two fragments is liable to become an ion.

19) D. P. Stevenson, *Discuss. Faraday Soc.*, **10**, 35 (1961).
20) M. Saito, I. Fujita, and K. Hirota, *J. Phys. Chem.*, **74**, 3147 (1970).