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TWO NEW TAXA FOR THE FLORA OF TURKEY

N. Demirkuş(1)

SUMMARY

Two new taxa for the flora of Turkey (Delphinium crispulum Rupr./ Ranunculacea and Polygonatum sibiricum Redouté / Liliaceae) have been described in this paper.

Key Words: Delphinium, Polygonatum.

TÜRKİYE FLORASI İÇİN İKİ YENİ TAKSON

ÖZET

Bu makalede, Türkiye Florası için iki yeni takson (Delphinium crispulum Rupr./ Ranunculaceae and Polygonatum sibiricum Redouté / Liliaceae) tanımlanmıştır.

Anahtar Kelimeler: Delphinium, Polygonatum.

INTRODUCTION

These plants were collected in 1984-1986, during our floristic study in the provinces of Kars. The taxa were checked from related references [1,7]. The specimens are kept in the Herbarium of Hacettepe University, at the Department of Biology (HUB).

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RESULTS

RANUNCULACEAE (Düğünçiçeğigiller)

Delphinium crispulum Rupr. in Fl. Cuac; (1869) 34. Table 1, Figure 1.

A new species for the Flora of Turkey. Differs from Delphinium linearilobum (Trautv.) Busch by its densely pilose follicles, longer spurs and narrower leaf lobes. Flowering time, July-August [1,2,3,4,5].

Type: In Leningrad.

Habitat: In high mountain meadows on stony soil and on moving taluses in the alpine zone.

A9 Kars: Göle, Balçeşme meadows, Pinus sylvestris forest, 2100-2300 m, 16.8.1984, Demirkuş, 2693 a.

Geographical Distribution: Caucasus.

Table 1. Comparison of Diagnostic Characters of D.crispulum and D.linearilobum.

Characters	D.crispulum	D.linearilobum
Spurs	1.1-1.5 cm long	0.5-1 cm long
Middle leaf segment base	2-8 mm broad	2-20 mm broad
Follicles	densely pilose	tomentose

LILIACEAE (Zambakgiller)

Polygonatum sibiricum Redouté, Lil. VI (1912) 314; Ldb. Fl. Ross. V, 124; Table 2, Figure 2.

A species new for Turkey is easily distinguished from P. sewerzowi Rgl. by its glabrous filament and smaller leaves.

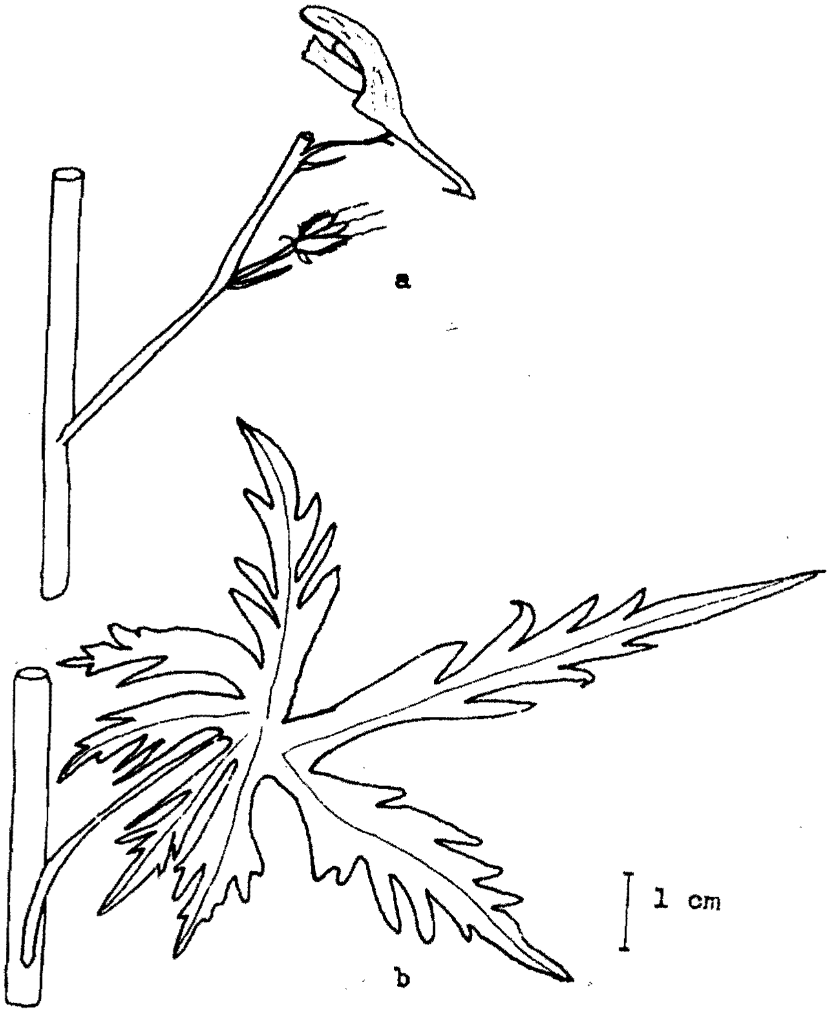

Figure 1. Delphinium crispulum Rupr.
a. flowers and follicles
b. leaves

Flowering time, May (6-7).

Type: In Genova.

Habitat: Woods.

A9 Kars: Posof, Gönülaçan Villages forest, 1900-2200 m,
8.5.1986, Demirkuş, 3488.

Geographical Distribution: East Sibaria.

Table 2. Comparison of Diagnostic Characters of P.sibiricum and P.sewerzowi.

Characters	P.sibiricum	P.sewerzowi
Plants	40-55 cm tall	50-70 cm tall
Upper leaves whorls	4-6	3-4
Leaves	5-8x0.35-0.6 cm	9-13x1.5-2.5 cm
Verticillasters	6-7 flowered	2-3 flowered
Filaments	glabrous	glandular-margined

In our plant specimens; peduncles 2.5-7 mm pedicels 0.5-2.7 mm, flowers 8-9.5 mm.

These characters have not been given in the flora of USSR [7].

ACKNOWLEDGEMENTS

I should like to thank to Hacettepe University Research Council, The Scientific and Technical Research Council of Turkey and The Forest Research Council of Turkey for their financial support.

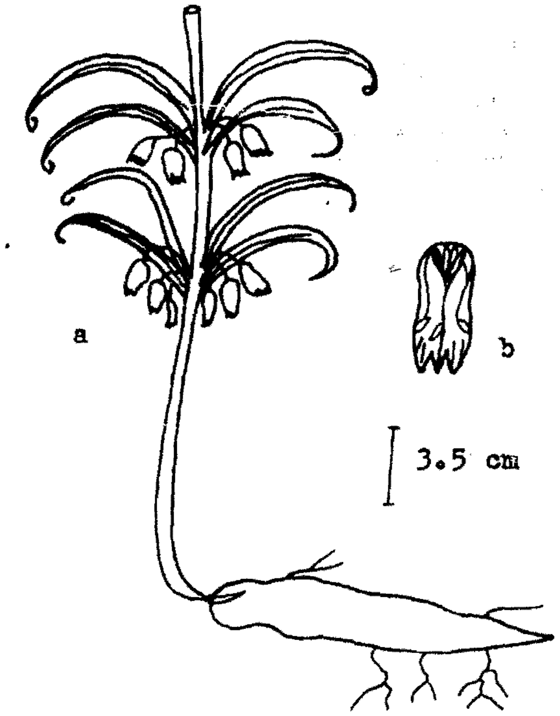

Figure 2. Polygonatum sibiricum Redouté
a. stem and leaves
b. flower in section

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DETERMINATION OF THE IONIZATION AND APPEARANCE POTENTIALS OF METHYL-, DIMETHYL-, AND TRIMETHYL AMINES AND INTERPRETATION OF THEIR FRAGMENTATION MECHANISMS

İ. T. Özgen(1), B. Salih(2) and E. Aydınlar(2)

SUMMARY

For the measurement of ionization potentials (I.P.) and appearance potentials (A.P.) with a mass spectrometer many parameters of the instrument must be precisely controlled, and big amount of data must be quickly recorded and saved and later processed. The most suitable way to fulfill this is to connect a computer to the mass spectrometer. This leads to better I.P. and A.P. results and better interpretation of results due to computer processing.

In this study methyl-, dimethyl-, and trimethyl amine data were obtained and processed by a computer which was coupled with the mass spectrometer. More precise and original data are obtained.

Key Words: Ionization potentials and Appearance potentials, Mass spectrometric fragmentation of amines.

METİL, DİMETİL VE TRİMETİL AMİNLERİN İYONLAŞMA VE GÖRÜNÜM POTANSİYELLERİNİN TAYİNİ VE PARÇALANMA MEKANİZMALARININ YORUMU

ÖZET

Bu çalışmada, etil-, dietil- ve trietil aminlerin iyonlaşma ve görünüm potansiyelleri tayin edilerek, parçalanma mekanizmalarının yorumu yapılmıştır. İyonlaşma ve görünüm potansiyellerinin tayini, VARIAN MAT CH7 model kütle spektrometresi ile tayin edilmiştir. Kütle spektrometresi ile hızlı ve duyarlı verilerin elde edilmesi için sisteme IBM PC uyumlu bilgisayar ve elektron enerjisinin 10 meV (mili elektron volt) aralıklarla değişimini sağlayan 4.5 digitlik bir elektron enerji kontrol ünitesi bağlanmıştır. Elde edilen sonuçların daha sağlıklı değerlendirilebilmesi için iyonlaşma verim eğrilerinden iyonlaşma ve görünüm potansiyellerinin bulunmasında, polinomial regresyon kullanılmış ve sonuçlar literatürde bulunan bazı verilerle karşılaştırılmıştır. İyonlaşma ve görünüm potansiyelleri ve klastogramlardan yararlanılarak incelenen bileşiklerin parçalanma mekanizmaları (oluşan türlerin hangi yapıdan ne gibi bir parçalanma ile oluştuğu) hakkında bazı önemli bilgiler elde edilmiştir.

Anahtar Kelimeler: İyonlaşma potansiyeli ve görünüm potansiyeli, Aminlerin kütle spektrometrik parçalanmaları.

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1. INTRODUCTION

Determination of I.P. and A.P. with a mass spectrometer is possible by obtaining ionization efficiency curves (I.E.C.). I.E.C.'s are curves drawn as a function of ion current versus electron energy. Determination of treshold values (I.P. and A.P.) from the I.E.C.'s is made by comparing the I.E.C. of sample ion by the I.E.C. of a reference ion.

If the I.P. of the sample ion is near to the I.P. of the reference ion, determination of the I.P.'s become easier. I.P.'s are evaluated by the interpretation of I.E.C.'s. Various methods have been improved for the interpretation of I.E.C.'s. Some of these methods are : linear extrapolation technique [1], vanishing current technique [2], semi logarithmic technique [3], and extrapolated voltage differences technique [4].

In all of these techniques treshold regions of the curves where the measured signals are low, are used for interpretation. Because the measured signals are low, signal/noise (S/N) ratios in the data are small and the errors in the results increase. To find the intersection point of the I.E.C.'s with the energy axis (which gives the numerical value of I.P. or A.P.) more accurately a polynomial was fitted to the I.E.C.'s. The degree of the polynomial was selected as 11'th degree. When a polynomial smaller than this degree was selected the goodness of fit decreased, and when a polynomial bigger than this degree was selected there was not a distinct improvement in the goodness of fit. A polynomial of 11'th degree can be expressed with the following equation.

$$f(x) = b_0 + b_1 x + b_2 x^2 + b_3 x^3 + \cdots\cdots\cdots + b_{11} x^{11} \qquad (1)$$

In the ideal case the degree of a polynomial is limited by the number of data. In general the degree of the applied polynomial is related to the number of data as given in the following equation.

$$M < 2 \times \sqrt{N} - 1 \qquad (2)$$

In the equation M represents the degree of polynomial, and N represents the number of data. In our experiments the minimum number of data was 500, so there was not any boundary in selecting an 11'th degree polynomial.

Fig 1, shows the curve obtained by applying 11'th degree polynomial to the ionization efficiency data of methyl amine. As seen in the Figure scatter due to experimental insufficiency is smoothed by the application of the polynomial.

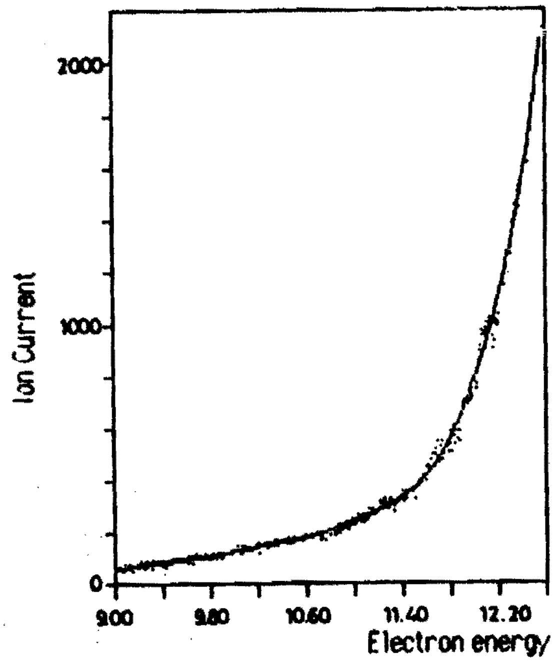


Figure 1. Applying polinomial regression on ionization efficiency curve.
.... experimental data, _______ fitted data.

After the application of data to the polynomial the b values in the polynomial was calculated and then the x values which makes the f(x) function zero (roots of the polynomial) were determined by Newton-Rapson method. The smallest value in the roots of the polynomial was found as the I.P. for the molecular ion or as the A.P. for the fragment ion. However this method was only used for the determination of I.P.'s or A.P.'s, no information can be obtained about the fine structure in the molecule with this technique.

2. TECHNIQUE OF MEASUREMENT

Experimental studies were made by a CH7 model VARIAN MAT mass spectrometer coupled with a IBM PC compatible computer. The mass spectrometer has a magnetic field analyser, a faraday cage detector and an electron impact ion source. Both the mass spectrometer can be controlled and the stored data can be processed by the computer. The system is schematically shown in Fig 2.

The computer uses a 14 bit analog to digital (ADC) converter with 16 channels and a 14 bit digital to analog (DAC) converter.

The electron energy control unit has a 4.5 digit display and the electron energy range is 0-105 volts. During the experiments the electron energy has to be changed in small intervals and measured accurately. Our electron energy control unit was designed for this purpose and could change electron energy in 10 meV intervals which was quite satisfactory.. Smaller intervals could also be set but it was omitted because experiment times increased considerably in that case.

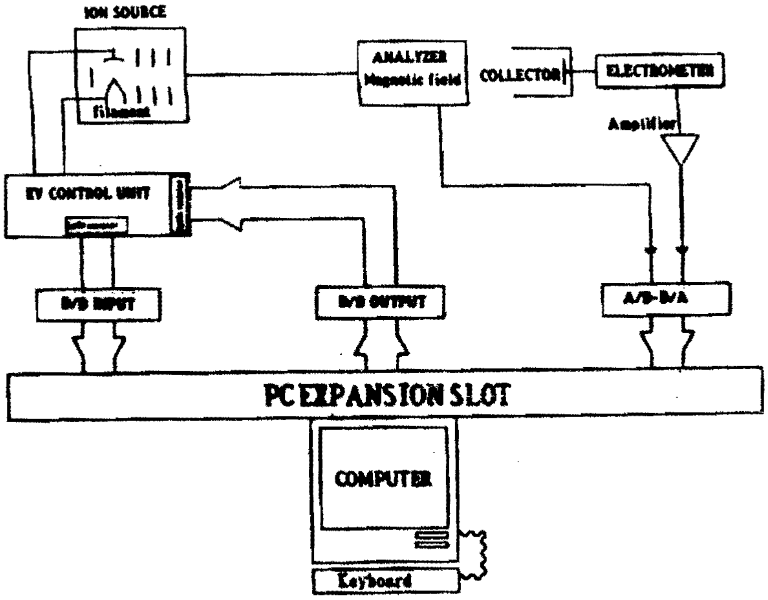


Figure 2. Mass spectrometer and connected systems.

The ionization efficiency data were collected by starting the measurements 2-3 volts below the treshold values, and by integrating each ion current for 3 seconds while changing electron energy at 10 meV (0.01 eV) intervals. After every energy change 1 second interval was given for the filament to attain equilibrium. In every experiment approximately 10 eV intervals were scanned.

3. FORMATION OF THE CLASTROGRAMS

I.P.'s of many organic compounds are between 7-15 eV. When fragment ions are detected with respect to the molecular ion, it is seen that percent intensity of the molecular ion decreases with appropriate fragmentation processes. As the electron energy is increased the molecular ion becomes more energetic, and when enough energy is attained, with suitable interactions, fragmentation occurs and relative intensities of fragment ions increase.

The term "clastogram" is used for expressing the changes in fragmentation with increased ionization energy [5]. This is a total graphical representation of ion currents versus electron energy. Clastograms prove to be more useful to explain reaction mechanizms of molecules [6]. In our study, clastograms of methyl-, dimethyl-, and trimethyl amines were drawn. Mass spectra at various energies were taken to get the data for the clastrograms , then percent intensities of various ion currents compared to total ion current were calculated and plotted. Figures 3., 4. and 5. show the clastrograms of methyl-, dimethyl-, and trimethyl amines.

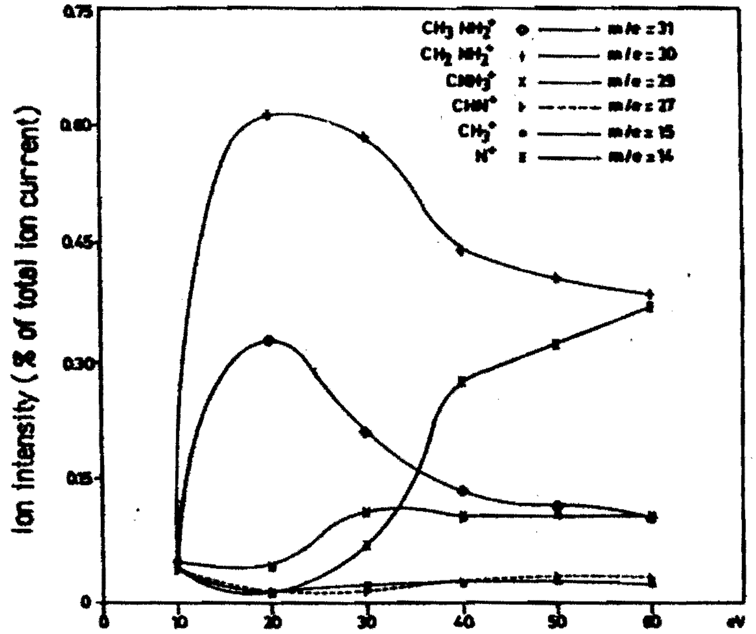


Fig 3. Clastrogram of methyl amine

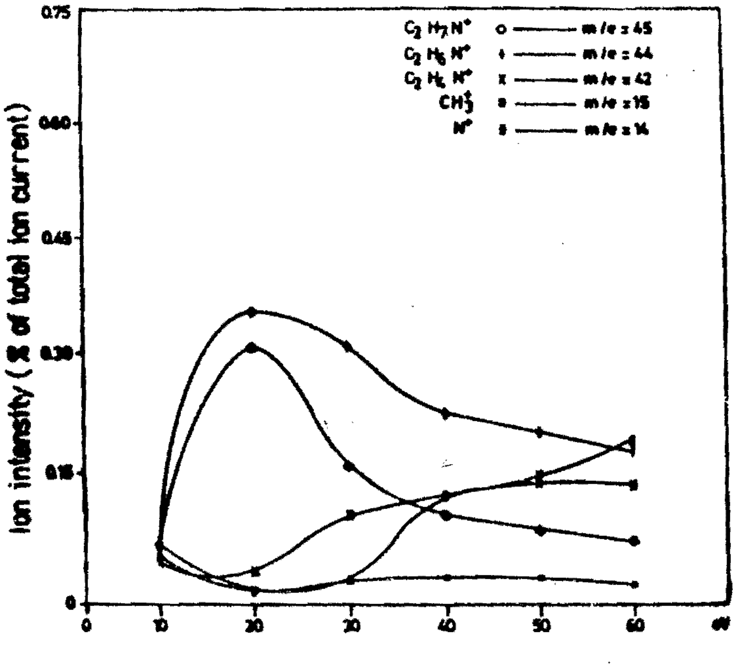


Fig 4. Clastrogram of dimethyl amine

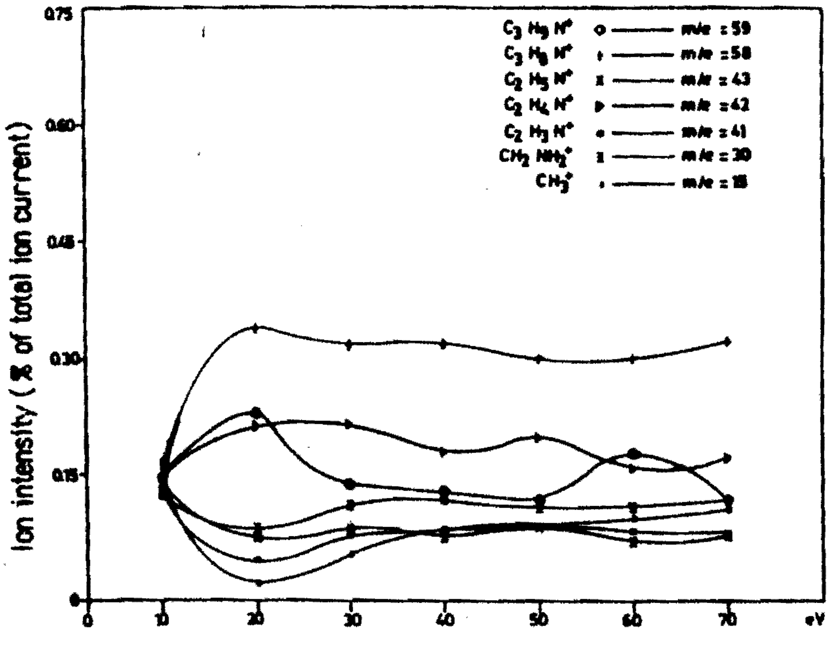
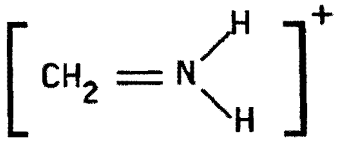


Fig 5. Clastrogram of trimethyl amine

4. EVALUATION OF FRAGMENTATION MECHANIZMS

Interpretation of mass spectrometric fragmentation of methyl amine

m/e = 30 peak (M-1) (A.P. =10.14 eV)



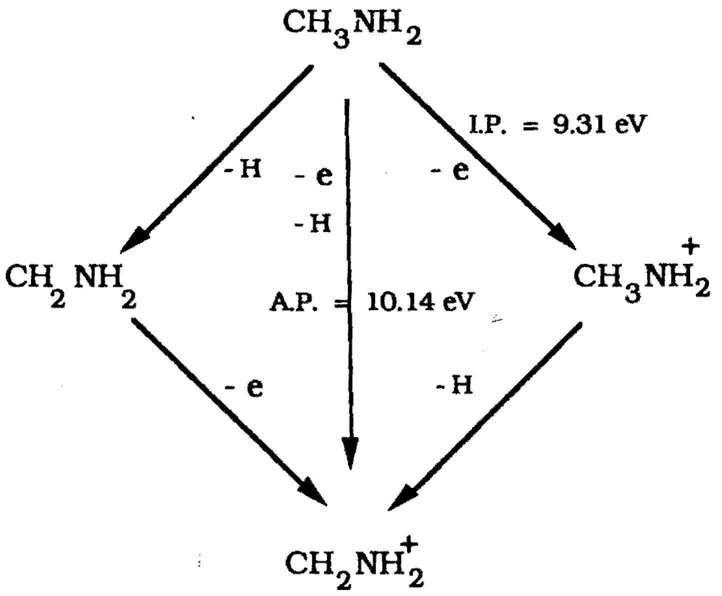
Formation of (M-1) peak is due to the breaking of a hydrogen from the molecule. This hydrogen breaks off from the methyl group. In reality the C—H bond energy is bigger than N—H bond energy (D(C—H) = 99 kcal/mol D(N—H) = 93 kcal/mol). Therefore one expects breaking off the hydrogen from the amine group first. But in this case, stability of the formed species effects the region where the hydrogen will break considerably. When hydrogen breaks off from the methyl group the stable species shown above is formed, so, hydrogen breaks off from the methyl group. To check this, mass spectrum of deuterated methyl compound CD_3NH_2 was inspected and (M-2) peak was found instead of (M-1) peak, which confirms the loss of hydrogen from the methyl group [7].

If we assume the formation of m/e = 30 peak ion as suggested above, the energetics of this reaction can be calculated as below:

for breaking bonds : D(C— H) = 4.29 eV energy required
for forming bonds : formation of (C=N) from (C— N) gives
6.37 - 3.17 = 3.20 eV energy.

Total energy for the formation of the ion :

A.P.($CH_2NH_2^+$) = I.P.($CH_3NH_2^+$)+ D(C— H) - D(C = N) = 9.31 + 4.29 -3.20 = 10.40 eV .



While breaking of D(C-H) bond requires 4.29 eV energy, 3.20 eV energy is given off during the formation of D(C=N) bond, therefore for the formation of $CH_2NH_2^+$ ion from · CH_2NH_2 radical energy calculations give:

I.P. (· CH_2NH_2) = A.P. ($CH_2NH_2^+$)- D(C-H) = 10.14 - 4.29 +3.20= 9.05 eV

m/e = 29 peak (A.P. =13.37)

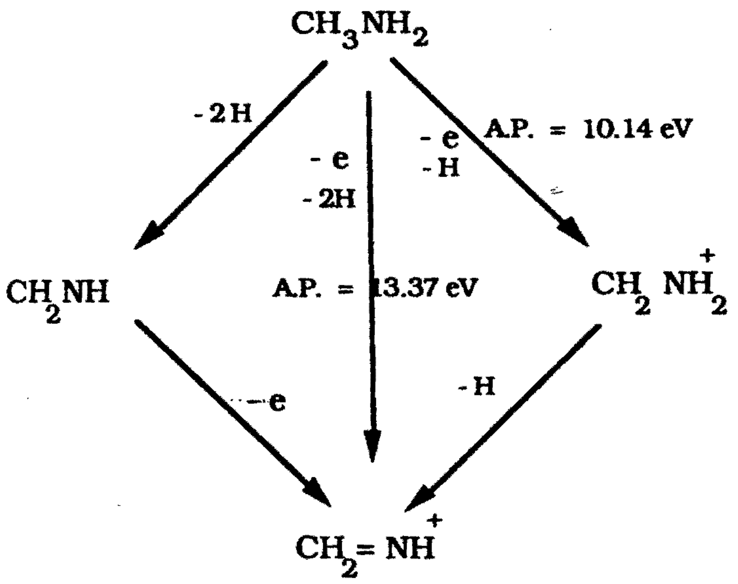
$$[H_2C{=}NH]^+$$

If we assume that mass 29 ion is formed as shown above from mass 30 ion, the energetics for the reaction can be explained as:

for breaking bonds : D(N— H) = 4.03 eV energy required since there are no new bonds formed, total energy change can be shown as:

A.P. (CH_2NH^+) = A.P. $(CH_2NH_2^+)$+ D(N— H) = 10.14 + 4.03 = 14.17 eV

This result shows us that mass 29 ion is formed from mass 30 ion by breaking off one of the hydrogens on the nitrogen atom.

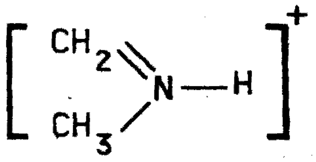


The thermodynamic cycle above shows that D(C-H)=4.29 is eV, and D(N-H)=4.03 is eV, and 3.20 eV energy will be released while the C=N bond will be formed. Therefore necessary energy for the formation of CH_2NH^+ ion from CH_2NH is:

I.P.(CH_2NH) = A.P.(CH_2NH^+) - D(C-H) - D(N-H) + D(C=N) = 13.37 -4.29-4.03 +3.20 = 8.25 eV .

Interpretation of mass spectrometric fragmentation of dimethyl amine

m/e = 44 peak (M-1) (A.P. = 10.29 eV)



44 mass ion is formed by breaking off the hydrogen from the methyl group in the dimethylamine group. Energetics for formation of m/e = 44 peak ion from the molecular ion can be calculated as below:
for breaking bonds : D(C— H) = 4.29 eV energy required
for forming bonds : formation of (C = N) from (C— N) gives
6.37 - 3.17 = 3.20 eV energy.
Overall energy change for the reaction:

A.P.($CH_3CH_2NH^+$) = I.P.($(CH_3)_2NH$) + (4.29-3.20) = 8.75 + 1.19 = 9.94 eV dir.

$$\begin{tikzcd}
 & (CH_3)_2NH \arrow[dl, "-H"'] \arrow[dr, "-e", "I.P. = 8.75\ eV"'] \arrow[dd, "-e\ -H\ A.P. = 10.29\ eV"] & \\
CH_3CH_2NH \arrow[dr, "-e"'] & & (CH_3)_2NH^+ \arrow[dl, "-H"] \\
 & CH_3CH_2NH^+ &
\end{tikzcd}$$

The thermodynamic cycle above shows that D(C-H) needs 4.29 eV, and 3.20 eV energy will be released while the C=N bond will be formed. Therefore necessary energy for the formation of $CH_3NHCH_2^+$ ion is:

I.P.(CH_3NHCH_2) = A.P.($CH_3NHCH_2^+$) - D(C-H) + D(C=N)= 10.29 - 4.29 +3.20 = 9.20 eV

m/e = 42 peak (A.P. = 11.16 eV)

$$[H_2C = N = CH_2]^+$$

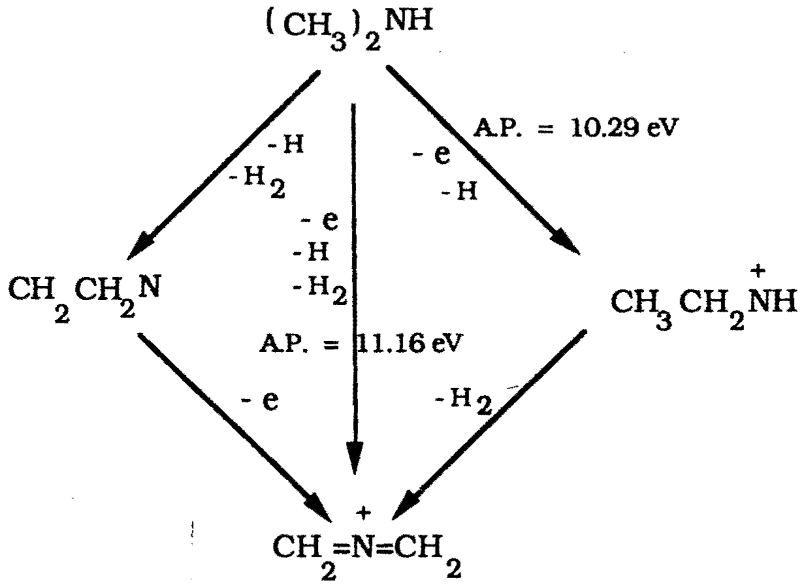
It can be assumed that 42 mass ion is formed from 44 mass ion. One hydrogen from the methyl group and one hydrogen from nitrogen should leave the molecule for this formation. On the other hand released hydrogen atoms can form an H_2 molecule. Energy calculations can be shown as:

for breaking bond : D(C— H) = 4.29 eV, and D(N — H) = 4.03 eV
energy required
for forming bonds : formation of (C = N) from (C – N) gives
6.37 - 3.17 = 3.20 eV energy. Therefore

A.P.($H_2C = N = CH_2^+$) = A.P.($CH_3NH - CH_2^+$) + (4.29 + 4.03 - 3.20)
= 15.41 eV

This value is much bigger than the experimental value. Therefore we can assume that released hydrogen atoms will form an H_2 molecule. If the energy released during the formation of the H_2 molecule is substracted from the above value we get the real A.P. for the ion above (15.41 - 4.51 = 10.90 eV).

This value of 10.90 eV agrees well with the measured value. Furthermore clastogram of dimethyl amin in Figure 4 also shows that when relative intensity of 44 mass ion decreases, relative intensity of 42 mass ion increases which also confirms that mass 42 ion is formed from mass 44 ion.



The thermodynamic cycle above shows that 2xD(C-H) needs (2x4.29) 8.58 eV and one D(N-H) bond cleavage needs 4.03 eV energy and (2x3.20) 6.40 eV energy will be released while two C=N bonds will be formed and 4.51 eV energy will be released when one mole of H-H will be formed. Therefore necessary energy for the formation of $CH_3NHCH_2{}^+$ ion is:

I.P.(CH_2NCH_2) = A.P.($CH_2NCH_2{}^+$) + (2 x 3.20) +4.51 - (8.58 + 4.03)
= 9.46 eV

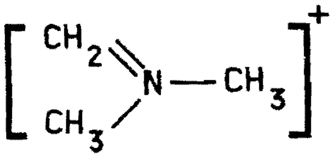
m/e = 15 peak (A.P. 13.22 eV)

$$[CH_3]^+$$

No rearrangement and new bond forming is necessary for the formation of this ion.

Interpretation of mass spectrometric fragmentation of trimethyl amine

m/e = 58 peak (M-1) (A.P. = 9.12 eV)



58 mass ion is formed by the cleavage of one of the hydrogens from one of the methyl groups in the molecular ion. Energy calculations can be shown as:

for breaking bond : D(C – H) = 4.29 eV energy required
for forming bonds : formation of (C = N) from (C–N) gives 6.37 - 3.17 = 3.20 eV energy. Therefore

A.P.[$(CH_3)_2NCH_2^+$] = I.P.[$(CH_3)_3N^+$] + D(C-H) - D(C =N) = 8.09 + (4.29 - 3.20) = 9.18 eV

$$\begin{tikzcd}
 & (CH_3)_3N \arrow[dl, "-H"'] \arrow[dr, "-e"', "\text{I.P.} = 8.90\ \text{eV}"] \arrow[dd, "\begin{array}{c}-e\\-H\\\text{A.P.} = 9.12\ \text{eV}\end{array}"] & \\
(CH_3)_2CH_2N \arrow[dr, "-e"] & & (CH_3)_3\overset{\cdot+}{N} \arrow[dl, "-H"'] \\
 & (CH_3)_2CH_2\overset{+}{N} &
\end{tikzcd}$$

The thermodynamic cycle above shows that D(C-H) needs 4.29 eV and 3.20 eV energy will be released while a C=N bond will be formed . Therefore necessary energy for the formation of $(CH_3)_2NCH_2^+$ ion is:

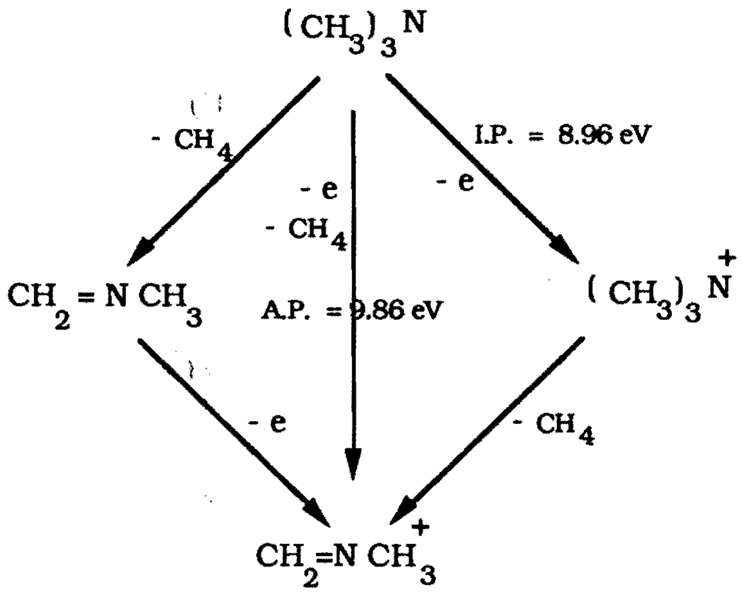
I.P.$[(CH_3)_2NCH_2]$ = A.P.$[(CH_3)_2NCH_2^+]$ - D(C-H) + D(C=N) = 9.12 - 4.29 + 3.20 = 8.03 eV

m/e = 43 peak (A.P. = 9.86 eV)

$$[H_2C{=}N{-}CH_3]^+$$

Two probabilities can be thought for the formation of mass 43 ion. First, the ion can be formed by the separation of methane from trimethyl amine, and second, separation of a methyl group from mass 58 ion. The clastogram in Figure 5 confirms that the second probability is valid. As seen in the clastrogram, the intensity of mass 43 peak increases as the intensity of mass 58 peak decreases. If we assume that the methyl group separates from the mass 58 ion, the energy calculations can be shown as below:

for breaking bond : D(C – N) = 3.17 eV energy required
Since no new bonds are formed,



A.P.($CH_2NCH_3^+$) = A.P.(($(CH_3)_2CH_2N^+$) + D(C-N) = 9.12 + 3.17 = 12.29 eV

The thermodynamic cycle above shows that D(C-N) needs 3.17 eV and D(C-H) needs 4.29 eV energy for breaking but 3.20 eV energy will be released while a C=N bond will be formed and 4.29 eV energy will be released while a C-H bond will be formed during the formation of methane. Therefore necessary energy for the formation of $CH_2NCH_3{}^+$ ion is:

I.P.(CH_2NCH_3) = A.P.($CH_2NCH_3^+$) - D(C-N) - D(C-H) + D(C=N) + D(C-H)

= 9.86 - 3.17 - 4.29 + 3.20 + 4.29 = 9.99 eV

m/e = 42 peak (A.P. = 9.81 eV)

$$[H_2C = N = CH_2]^+$$

We think that mass 42 ion is formed by the separation of methane from mass 58 ion. The trimethyl amin clastogram in Figure 5 confirms our assumption. As seen in the clastrogram, the intensity of mass 42 peak increases as the intensity of mass 58 peak decreases. Energy calculations can be shown as:

for breaking bonds : D(C - N) = 3.17 eV, and D(C - H) = 4.29 eV energy required

for forming bonds : formation of (C = N) from (C- N) gives

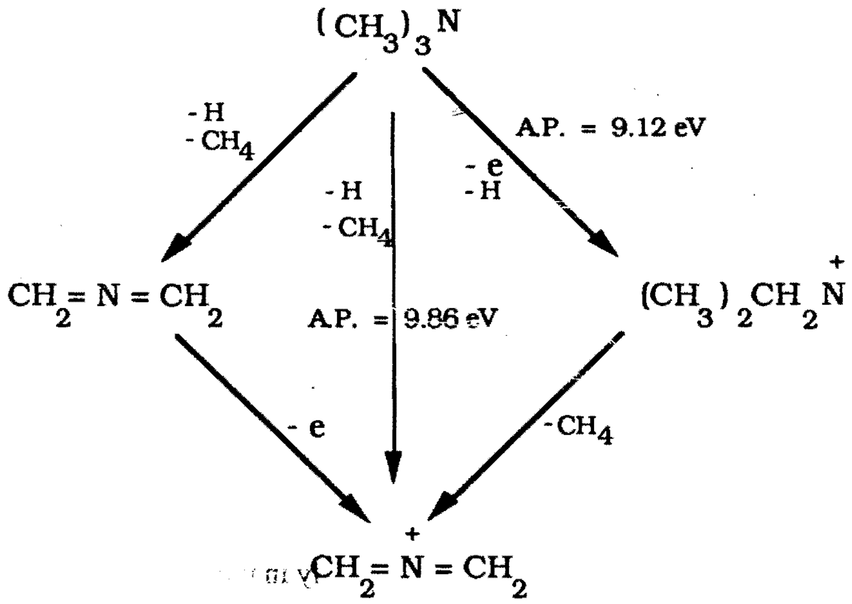
6.37 - 3.17 = 3.20 eV energy and 4.29 eV energy will be released while a C-H bond will be formed during the formation of methane. Therefore

A.P.($CH_2NCH_3^+$) = A.P.[(CH_3)2NCH_2^+] - D(C-N) - D(C-H) + D(C =N) + D(C-H)

= 9.17 - 3.17 - 4.29 + 4.29 + 3.20 = 9.12 + 0.03 = 9.15 eV

If we assume that the methyl group and hydrogen do not separate from the mass 58 ion as methane, energy calculations would give :
$9.09 + 4.29 = 13.38$ eV .

However this value is much higher than the experimentally found value, which also confirms that methane separates from the mass 58 ion.



The thermodynamic cycle above shows that 2D(C-H) needs (2x4.29) 8.58 eV and D(C-N) needs 3.17 eV but (2x3.20) 6.40 eV energy will be released while 2 C=N bond will be formed and 4.29 eV energy will be released while a C-H bond will be formed during the formation of methane. Therefore necessary energy for the formation of $CH_2NCH_2{}^+$ ion is:

$I.P.(CH_2NCH_2) = A.P.(CH_2NCH_2{}^+) - 2D(C\text{-}H) - D(C\text{-}N) + D(C\text{-}H) + 2D(C{=}N)$
$I.P.(CH_2NCH_2) = 9.86 - 8.58 - 3.17 + 4.29 + 6.40 = 8.80$ eV

m/e = 30 peak (A.P. = 11.58)

$$\left[CH_2 = NH_2\right]^+$$

5. RESULTS AND DISCUSSION

In this study ionization potentials of methyl-, dimethyl-, and trimethyl amines and appearance potentials of their fragment ions were determined. In order to determine the I.P.'s and A.P.'s , polynomial regression (11'th degree) was applied to the ionization efficiency data. After the calculation of the polynomial constants, I.P.'s and A.P.'s were determined from the roots of the polynomial. The I.P.'s and A.P.'s found in this way, are listed with the literature values for comparison, in Tables 1., 2. and 3. Our values are given with their standard deviations since they are the averages of 6-15 independent experiments.

Table 1. I.P. and A.P. values of methyl amine and its fragment ions (eV).

	This Study	Other Studies	
Mass No	I.P. or A.P.	Ref. value	Method
31	9.31 ± 0.04	9.45	EI (9)
		8.99	PE(8)
30	10.14 ± 0.01	10.55	EI (9)
		10.82	EI (8)
29	13.37 ± 0.08	13.30	EI (8)

Table 2. I.P.and A.P. values of dimethyl amine and its fragment ions (eV).

	This Study	Other Studies	
Mass No	I.P. or A.P.	Ref. value	Method
45	8.75 ± 0.08	8.83	EI (9)
		8.24	PI (8)
44	10 .29 ± 0.05	9.41	EI (9)
		10.50	EI (9)
42	11.16 ± 0.07	10.55	EI (9)
15	13.22 ± 0.16	10.10	RPD (7)

Table 3. I.P.and A.P. values of trimethyl amine and its fragment ions(eV).

	This Study	Other Studies	
Mass No	I.P. or A.P.	Ref. value	Method
59	8.09 ± 0.02	7.95 8.44 7.80	PI (9) EI (9) PE (8)
58	9.12 ± 0.07	10.55 9.80	EI (9) RPD (8)
43	9.86 ± 0.01		
42	9.81 ± 0.03		
30	11.58 ± 0.01		
15	13.32 ± 0.10		

6. CONCLUSION

As is seen from the tables, there is little electron impact study in the literature. There is even no study on fragment ions at all. Some of the ions and fragments we studied have been studied before, and our A.P. and I.P. results are in good agreement with the results in the literature. However our results in general, have lower values than the values given in the literature . Some of our results are original and have not been studied before. These better results we think, is both due to the experimental set up and to the data processing procedure. As we can control the functions of the mass spectrometer with a computer we can get more precise results with satisfactorily small intervals and number of our data is enough for processing with the computer. Resolution in finding the intersection point of our ionization efficiency curves with the energy axis gave improved I.P. or A.P. results due to the polynomial technique we used .

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