Structural elucidation of organic contaminants by chemical ionisation mass spectrometry

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Abstract. The PI-CI mass spectra formation for a new family of aromatic amines, with general formula: \(R_1\)-Ph-NH-Ph-\(R_2\) is discussed in correlation with the \(R_1\) and \(R_2\) structure. The compounds where isolated from some environmental samples by GC/MS technique. The characteristic ions are produced by rearrangement processes involving olefin and alkane neutral molecule elimination from \([M+H]^+\) and sole olefin molecule elimination from \([M+C_2H_5]^+\).

1. Introduction
In the chemical ionization mass spectrometry (CI-MS), the ionization of a substance takes place by ion-molecule reactions rather than electron impact (EI) or field ionization (FI). The CI spectrum is different from the spectra produced by other ionization techniques and the analytical and scientific utility of the method stems from the unique character of the chemical ionization spectra. By comparison, the molecule-ions initially formed by EI processes are odd-electron ions, whose decomposition is influenced by the presence of the odd electron. Evidently, the ions initially formed by even-electron CI processes may be expected to decompose by rather different networks of pathways. Another reason for difference is the fact that whereas in EI ionization, the energy transfer distribution can include values with 10 eV above ionization potential, the energy transfer in CI processes exceeds only 5 eV [1]. As a consequence, complementary structural information can be obtained by CI processes.

The ion decomposition depends only on its internal energy (described by probability function \(P(E)\)) and of the rate constant \(k(E)\) of the particular reaction. Decompositions of molecular ions in the mass spectrometer are generally produced by two ways: \(i)\) simple cleavage of a bond, and \(ii)\) by prior rearrangement of atoms and elimination of neutral molecule. In the rearrangement reaction two new bonds are formed offsetting the energy required to cleave other two. The critical energy for a reaction involving only a simple bond cleavage is higher. Based on this reason it results that by CI the reactions involving rearrangement of atoms are predominant relative to the simple fission reactions [2].

2. Results and discussion
The paper discusses the positive ionization CI (PI-CI) mass spectra (methane as reactive gas) for five members from a new family of aromatic amines shown in table 1. The compounds where isolated from some environmental samples by GC/MS technique[3]. The EI mass spectra early reported[3] are
dominated of ions [M-15]+ and [M-71]+, produced by simple cleavage (benzylic bond), corresponding to elimination of radical –CH₃ and –C₅H₁₁ respectively from R.

**Table 1.** The studied compounds structure R₁-Ph-NH-Ph-R₂.

| Compound | R₁  | R₂  | Symbol |
|----------|-----|-----|--------|
| 1        | H   | C(CH₃)₃| (0,4)  |
| 2        | C(CH₃)₃| C(CH₃)₃| (4,4)  |
| 3        | H   | C(CH₃)₂C₅H₁₁| (0,8)  |
| 4        | C(CH₃)₃| C(CH₃)₂C₅H₁₁| (4,8)  |
| 5        | C(CH₃)₂C₅H₁₁| C(CH₃)₂C₅H₁₁| (8,8)  |

2.1. Mechanism of production of ions visible in PI-CI mass spectra

2.1.1. Pseudo molecular ion

The principal reagent ions formed from methane at 1 torr are CH₅⁺ and C₅H₁⁺ [1]. The two types of pseudo molecular ions are produced by interaction of the neutral compounds with different types of ions resulting from reactive gas:

- **R₁-Ph-NH-Ph-R₂ + CH₅⁺ → R₁-Ph-N⁺H₂-Ph-R₂ [M+1]⁺ (proton transfer)**
- **R₁-Ph-NH-Ph-R₂ + C₅H₁⁺ → R₁-Ph-HN(C₂H₅)-R₂ [M+29]⁺ (electrophilic addition)** [4]

2.1.2. Fragment ions

Having [M+1]⁺ ion as precursor, two reactions of decomposition are visible:

a. Rearrangement reaction involving an H transfer in a *four-membered transition state* and the elimination of *olefin* molecules of type [R-H] (C₄H₈, C₈H₁₆) depending of R₁ and R₂ structures. The difference in mass units relative to [M+1]⁺, Δ₁ is 56 an 112 respectively.

b. Rearrangement with H transfer also in a *four-membered transition state* and elimination of *alkane* molecule of type CH₄ or C₅H₁₂ depending of atom subgroups present in R₁ and R₂. Mass difference Δ₁ being 16 and 72 respectively.

c. From [M+29]⁺ only the olefinic molecules of type [R-H] (C₄H₈, and respectively C₈H₁₆) are eliminated after H transfer. The mass difference relative to [M+29]⁺, Δ₂₉ is also 56 and 112 corresponding to neutral elimination.

The mechanism of fragmentation of the ions [M+1]⁺ and [M+29]⁺ is shown in scheme I.

**Scheme I.** Fragmentation of the ions [M+1]⁺, r = H (a and b fragmentation) and [M+29]⁺, r = C₅H₁⁺ (only c fragmentation).
Figure 1. PI-CI mass spectrum of Compound 1(0,4). The ions $a$ and $c$ correspond to olefin $C_4H_8$ elimination but the ion $b$ to alkane $CH_4$ elimination from $R$.

The mass spectrum of compound 1 is shown in figure 1. The mass spectrum presents three fragment ions: ion $a$, $m/z$ 170 (elimination of $C_4H_8$ from $[M+1]^+$) ion $b$, $m/z$ 210 (elimination of $CH_4$ from $[M+1]^+$) and ion $c$, $m/z$ 198 (elimination of $C_4H_8$ from $[M+29]^+$. The ions $a$ and $b$ are diagnostic ions for $R$. The difference between $[M+1]^+$ and $a$ as well as between $[M+29]^+$ and $c$ is the same ($\Delta_1 = \Delta_{29} = 56$) corresponding to neutral $C_4H_8$. The ion $b$ is a diagnostic ion for detailed structure of $R$. The difference $\Delta_i$ between $[M+1]^+$ and $b$ is 16 corresponding to atom group $CH_4$ as subgroup from $R$.

Figure 2. PI-CI Mass Spectrum of Compound 4 (4*,8). The type of ions are indicated by $a$, $b$ and $c$ and $a^*$, $b^*$ and $c^*$ for contribution of $R$ and $R^*$ respectively.
Table 2. Number of fragment ions related to molecular structure.

| Compound | $N_a$ | $N_b$ | $N_c$ | $N_t$ |
|----------|-------|-------|-------|-------|
| 1: (0,4) | 1, C(CH$_3$)$_3$ | 1, CH$_3$ | 1, C(CH$_3$)$_3$ | 3 |
| 2: (4,4) | 1, C(CH$_3$)$_3$ | 1, CH$_3$ | 1, C(CH$_3$)$_3$ | 3 |
| 3: (0,8) | 1, C(CH$_3$)$_2$C$_3$H$_{11}$ | 2, CH$_3$ + C$_3$H$_{11}$ | 1, C(CH$_3$)$_2$C$_3$H$_{11}$ | 4 |
| 4: (4,8) | 2, C(CH$_3$)$_2$+C(CH$_3$)$_2$C$_3$H$_{11}$ | 2, CH$_3$ + C$_3$H$_{11}$ | 2, C(CH$_3$)$_3$ + C(CH$_3$)$_2$C$_3$H$_{11}$ | 6 |
| 5: (8,8) | 1, C(CH$_3$)$_2$C$_3$H$_{11}$ | 2, CH$_3$ | 1, C(CH$_3$)$_2$C$_3$H$_{11}$ | 4 |

The mass spectrum of compound 4 (4*,8) is shown in figure 2. The type of ions is denoted by a, b, c and a*, b*, c*, originating from R and R* respectively. The number of fragment ions observed in mass spectrum are six: ion a, m/z 226, $\Delta_1=112$; c, m/z 254, $\Delta_2=112$; b$_1$, m/z 266, $\Delta_1=72$; a*, m/z 282, $\Delta_1=56$; c*, m/z 310, $\Delta_2=56$ and b$_2$, m/z 322, $\Delta_1=16$. The ions a, b, and c are diagnostic ions for R but a*, b* and c* are diagnostic ions for R*. The values $\Delta_1$ and $\Delta_2$ corresponding to detected ions are of 112 (elimination of C$_8$H$_{12}$ from R), 56 (elimination of C$_4$H$_9$ from R*) 72 (elimination of C$_5$H$_{12}$ as subgroup from R) and 16 (elimination of CH$_4$ as subgroup from R and R*).

3. Conclusions

The ions present in PI-CI mass spectra of compounds 1-5 are produced by rearrangement processes involving H atom transfer by a four membered transition state. Two type of ions were observed: the first one formed by elimination of olefin group with structure [R-H] and a second one produced by elimination of a paraffin group with structure [R$_i$+H]. $R_i$ being a subgroup of atoms from R. Between the number of peaks detected in PI-CI mass spectra and the structure of R groups the following correlations exist: $N_a$ (peaks a) = 1 x $N_R$ (R structures); $N_b$ (peaks b) = 1 x $N_{R_i}$ ($R_i$ structures); $N_c$ (peaks c) = 1 x $N_R$ (R structures). $N_t$ (total) = $N_a$ (peaks a) + $N_b$ (peaks b) + $N_c$ (peaks c). For compounds 1-5, a practical relation between total numbers of peaks observed in mass spectrum and R structures was established (table 2).

References
[1] Chapman J R 1985 Practical Organic Mass Spectrometry (Chichester: Wiley)
[2] McLafferty F W and Turecek F 1993 Interpretation of Mass Spectra (Mill Valley: University Science Books)
[3] Moldovan Z and Bayona J M 2000 Rapid Commun. Mass Spectrom. 14 379
[4] Moldovan Z Maldonado C and Bayona J M 1997 Rapid Commun. Mass Spectrom. 11 1077.