APPLICATION OF CSI-DIFF-MS SOFTWARE FOR IDENTIFICATION OF THE BEST QUANTUM CHEMICAL METHOD FOR 3- AND 4-NITROBENZOPHENONE DIMETHYLACETAL MOLECULES AND FRAGMENTATION IONS

APLICAREA PROGRAMULUI CSI-DIFF-MS LA STABILIREA METODEI CUANTOCHIMICE OPTIME PENTRU MOLECULELE SI IONII DE FRAGMENTARE AI DIMETILACETALILOR 3- SI 4-NITROBENZOFENONEI

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Abstract

In this work a new method to rapidly check the quantum chemical calculations methodologies is presented. This method is using the obtained mass spectrometry fragmentation experimental data. For this purpose were used the formation heat obtained from semi-empirical calculation methods such as AM1, MINDO3, MNDO, PM3, for the molecules and the ions resulted by fragmentation of 3- and 4- nitrobenzophenone dimethyl acetals, and also from the mass spectra of these two compounds and from the CSI-Diff-ms 1.2 software employed to differentiate between the mass spectra and to correlate the calculated thermodynamic data.

Keywords: nitrobenzophenone dimethyl acetals, aromatic position isomers, differential mass spectra, computational chemistry, heat of formation, quantum chemical semi empirical MO methods, AM1, MINDO3, MNDO, PM3

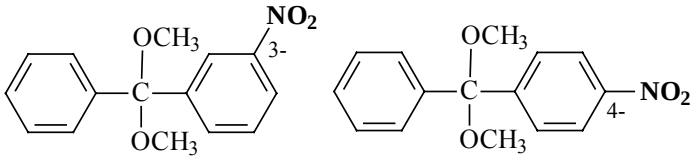
Introduction

The new technology: Chemical Structure Identification based on Differential Mass Spectra (CSI-Diff-ms) is related to the recently interdisciplinary field *"differential mass spectrometry"* and increases the efficiency of two chemical investigation methods, the mass spectrometry and the computational chemistry[1-4], in order to provide a new and revolutionary method. This method is used to identify[4]:

- the chemical structure of isomer substances with similar mass spectra;
- the best mathematical model, selected from a number of proposed mathematical models, that describes the kinetics and the thermodynamics of the ionization-fragmentation process inside the mass spectrometry system;
- the best set of heat of formation or activation energy for the analyzed fragmentations, selected from a number of proposed sets calculated with various quantum chemical calculation methods.

This method and software CSI-Diff-ms establish the correlation between the experimental data obtained through mass spectrometry with theoretical data offered by computational chemistry for the substances with extremely similarly structures, like isomers, and allows the identification of isomer substances based on mass spectra processing[4].

In this paper, is determined the best heat of formation set for molecules and fragmentation ions calculated with various quantum chemical calculations methods AM1, MINDO3, MNDO and PM3, using the mass spectra of two position aromatic isomers: 3- and 4- nitrobenzophenone dimethylacetals as etalon:



3- nitrobenzophenone dimethylacetal **4- nitrobenzophenone dimethylacetal**

Materials and methods

Mass spectra

Mass spectra were obtained using a GC Hewlett Packard 5890 with Detector MSD 5972, operating at 70eV, column HP-SM5, carrier gas He (1ml/min), with a probe temperature range between 50-275^{o}C, scan range, m/z 50-550. The tuning was performed using HP 5972 Standard Spectra AutoTune; standard PFTBA. The acetals were prepared by reaction of 3- and 4-nitrobenzophenones with methanol and dimethylsulfite under a continuous hydrogen chloride stream. The obtained compounds were characterized by ^{1}H-NMR, ^{13}C-NMR, IR spectroscopy, MS (EI) and by means of elemental analysis [5].

ΔH_f database

The molecules and fragmentation ions heats of formation (ΔH_f) database were calculated (Fig. 2). The geometries of the molecules and radicals were optimized with the field of forces MM+ and re-optimized with the semi-empirical method AM1, MINDO3, MNDO, PM3 [6-8], using the RHF operators for molecules or ions and UHF for the radical ions. The convergence limit SCF was 10^{-5}, with the accelerated convergence procedure. For the optimization of the geometries the conjugated gradient method – Polak-Ribiere[6,7], with a gradient RMS = 10^{-2} was used, the molecule being considered in vacuum.

Optimal semi empirical method

The CSI-Diff-ms 1.2. software was kindly provided for application purposes by the producing company BET2 Software[9]. With this software, using ΔH_f calculated database by HyperChem and etalons mass spectra, the probability of the sought isomers structures of these two isomers was calculated. The quantum chemical method which is used for the correct assignment of the structures with the highest probability was found to be the most appropriate method.

CSI-Diff-ms has the major advantage of permitting a fast data analysis and the possibility to be used even by non experts due to the simple steps easy to achieve. These steps are following[4]:

1. The input of similar mass spectra of two position aromatic isomers (Figure 1).

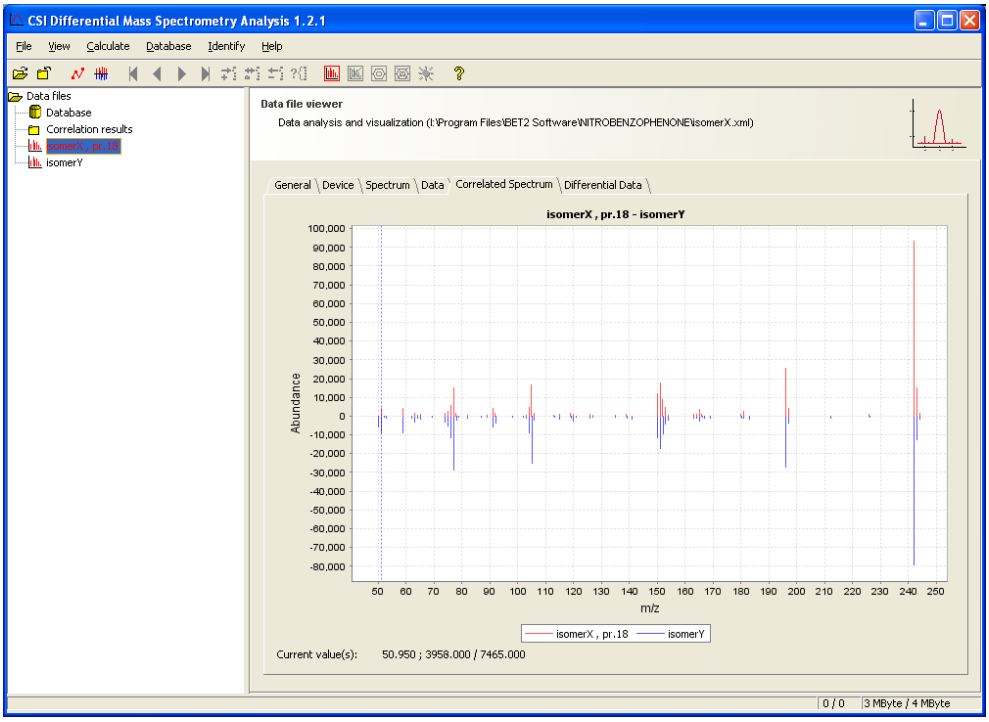


Figure 1. The reflected similar mass spectra of two etalons

2. The input of possible isomers, 3- and 4- nitrobenzophenone dimethylacetals, by using the command ″Select Ion Database Record″ of CSI-Diff-ms (Figure 2). In this way the thermodynamic data of the major ions (m/z 242, m/z 226, m/z 196, m/z 181, m/z 165 and m/z 150) are automatically loaded.

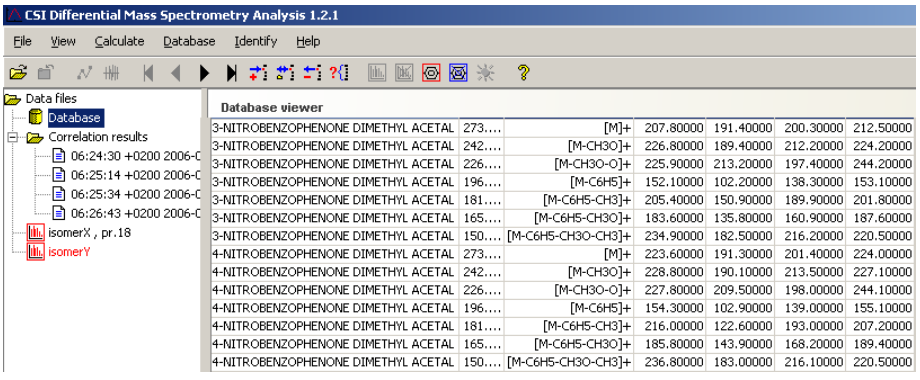


Figure 2. The input windows for isomers, fragmentation ions and their heats of formation

3. The selection of thermodynamic data set by choosing the desired/appropriate quantum-chemical method (Figure 3).

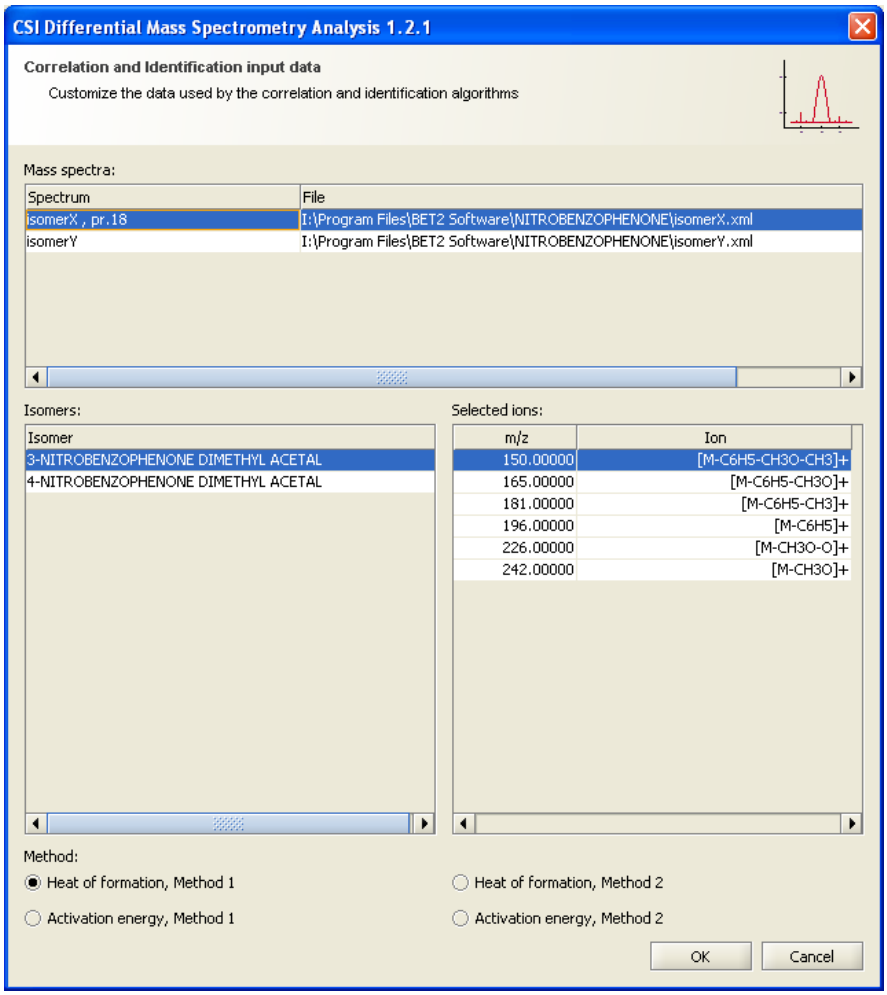


Figure 3. The window of the quantum chemical method selection

4. The settlement of the structure by using ″Calculate Probability″ command.

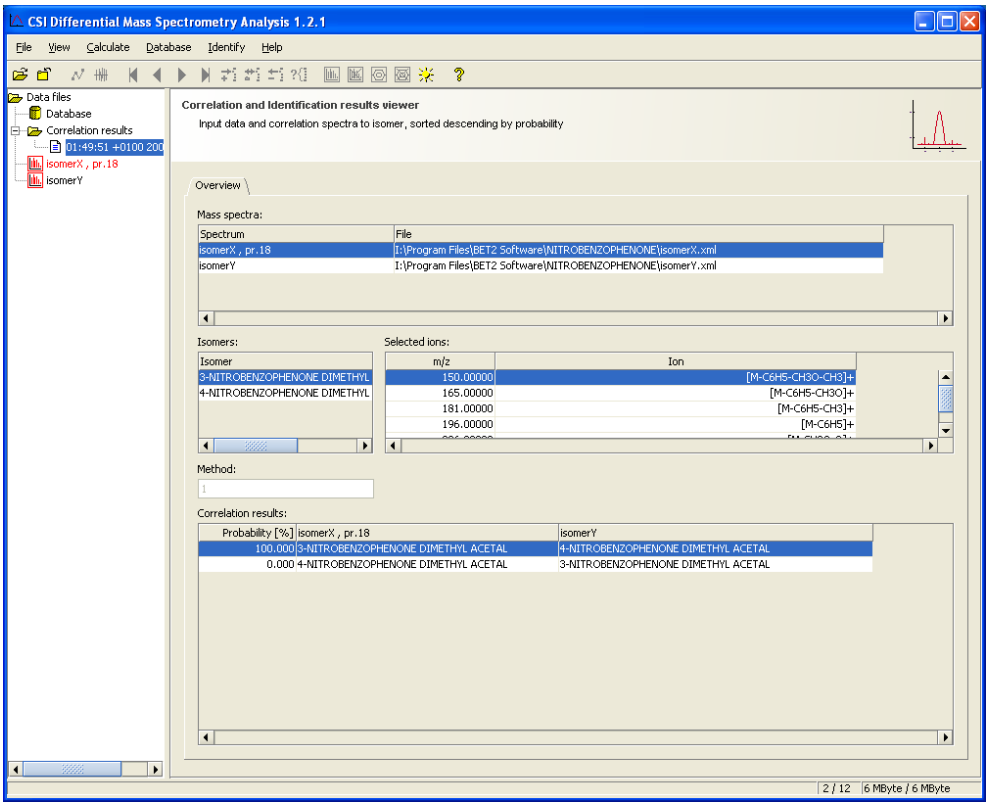


Figure 4. The probability window shows the percentage of structures assignment. If an identification structure probability is 100%, the probability is 0% for the inverse assignment

Results and discussions

Taking into account the research methodology, the probability of settlement of the structures of the two etalons becomes a quality indicator of the formation heats used from the database. This way, all four quantum chemical methods induce a correct assignment of the two structures (Table 1 and 2) but the best method in this case is AM1 because its correct assignment probability is 100%.

MINDO3 method was found to be less appropriate for 3- and 4-nitrobenzophenone dimethylacetals.

Table 1. Correct assignment

Etalon	Correct assignment	AM1	MINDO 3	MNDO	PM3
3-nitrobenzophenone dimethyl acetal	3-nitrobenzophenone dimethyl acetal	100 %	66%	83%	83%
4-nitrobenzophenone dimethyl acetal	4-nitrobenzophenone dimethyl acetal				

Table 2. Inverse assignment

Etalon	Inverse assignment	AM1	MINDO 3	MNDO	PM3
3-nitrobenzophenone dimethyl acetal	4-nitrobenzophenone dimethyl acetal	0%	33%	17%	17%
4-nitrobenzophenone dimethyl acetal	3-nitrobenzophenone dimethyl acetal				

Conclusions

The correct assignment of the structures using this novel protocol demonstrates the reliability of the used quantum chemical methods as well as the entire concept of differential mass spectra correlation with the formation heats of the fragments from the mass spectra.

To the best of our knowledge, for the first time a software platform, CSI-Diff-ms, offers the possibility to rapidly check by means of mass spectrometry the validity of the quantum chemical calculations, the proposed fragmentation mechanism as well as the identification of the analyzed structures from calculation data.

Abstract

Este prezentata o noua posibilitate de verificare rapida a metodelor de calcul cuantochimic prin folosirea datelor experimentale obtinute cu spectrometria de masa de fragmentare. S-au folosit in acest scop caldurile de formare calculate cu metodele OM semiempirice AM1, MINDO3, MNDO, PM3, pentru moleculele si ionii rezultati in spectrometrul de masa din dimetilacetalii 3- si 4- nitrobenzofenonei, spectrele de masa ale acestora precum si platforma software CSI-Diff-ms 1.2 necesara diferentierii spectrelor de masa si corelarea acestora cu datele termodinamice calculate.

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