

# Application of CSI-DIFF-MS software for identification of the best quantum chemical method for 2-, 3- and 4- nitrobenzophenone molecules and fragmentation ions

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## INTRODUCTION

The new technic, 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<sup>1-3</sup>, in order to provide a new and revolutionary method. This method is used to identify:

- 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 ionisation-fragmentation process inside the mass spectrometry system;
- the best set of heat of formation or activation energy for the analysed fragmentations, selected from a number of proposed sets calculated with various quantum chemical calculation methods [1].

This method and CSI-Diff-ms 3.1.1 software establish the correlation between the experimental data obtained through mass spectrometry with theoretical data offered by computational chemistry for the substances with extremely similar structures, like isomers, and allows the identification of isomer substances based on mass spectra processing [2]. In this paper, is determined the best heat of formation set for molecules and fragmentation ions calculated with various quantum chemical calculations methods: MINDO3, MNDO, AM1 and PM3, using the mass spectra of three position aromatic isomers: 2-, 3- and 4- nitrobenzophenone (Nbf) as etalon.

In a previous study [3,4], for the discrimination of the two position isomers, the correlation between the differential mass spectrum of the dimethylacetals of 3- and 4-nitrobenzophenones and the diagrams drawn with the heats of formation corresponding to the molecular and fragmentation ions, calculated with semiempirical quantum chemical methods have been used.

## EXPERIMENTAL

### 1. Mass spectrometry

Mass spectra were obtained using a GC Hewlett Packard 5890 with Detector MSD 5972, operating at 70eV, column HP-5MS, carrier gas He (1mL/min), with a probe temperature range between 50-275°C, scan range, m/z 50-550. The tuning was performed using HP 5972 Standard Spectra AutoTune; standard PFTBA.

### 2. Nitrobenzophenones samples

The nitrobenzophenones used have been synthesised by acylation of benzene with the chlorides of 2-, 3- and 4-nitrobenzoic acids in the presence of ferric chloride. They have been analysed by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR spectroscopy, MS (EI) and elemental analysis [6]. All three samples were analyzed under the same instrumental conditions.

### 3. ΔH<sub>f</sub> database

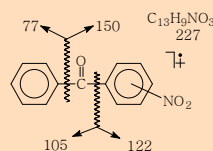
The molecules and fragmentation ions heats of formation (ΔH<sub>f</sub>) database were calculated. The geometries of the molecules and radicals were optimized with the field of forces MM+ and re-optimised with the semi-empirical method MINDO3, MNDO, AM1, PM3 [4,5], using the RHF operators for molecules or ions and UHF for the radical ions. The convergence limit SCF was 10<sup>-5</sup>, with the accelerated convergence procedure. For the optimisation of the geometries the conjugated gradient method – Polak-Ribiere, with a gradient RMS = 10<sup>-2</sup> was used, the molecule being considered in vacuum.

### 4. Optimal semi-empirical method

The CSI-Diff-ms 3.1.1 software was kindly provided for application purposes by the producing company BET2-Software [7]. With this software, using ΔH<sub>f</sub> calculated database by HyperChem and etalons mass spectra, the probability of the sought isomers structures of the 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.

## RESULTS

a) Comparative analysis of the electronic impact mass spectra (EI-MS) of the 2-, 3- and 4-Nbf isomers leads to the observation that the fragmentation of these compounds is similar (scheme 1).



Scheme 1

Table 1. The similarity of the Nbf mass spectra

Similarity (%)	2-Nbf	3-Nbf	4-Nbf
2-Nbf	100	67.71	71.18
3-Nbf	67.71	100	77.83
4-Nbf	71.18	77.83	100

b) The similarity of the mass spectra for the Nbf position isomers (table 1) showed a higher similarity between the spectra of 3- and 4- Nbf.

c) The formation heats values (table 2) are introduced in CSI-Diff-ms 3.1.1 database.

Table 2. The formation heats values (kcal/mol) of Nbf molecules and fragments, calculated with semi-empirical methods MINDO3, MNDO, AM1 and PM3

Structure	m/z	MINDO3			MNDO			AM1			PM3		
		2Nbf	3Nbf	4Nbf	2Nbf	3Nbf	4Nbf	2Nbf	3Nbf	4Nbf	2Nbf	3Nbf	4Nbf
M	227	8.00	6.59	6.38	34.37	31.63	31.60	28.97	24.92	24.93	12.75	9.15	9.15
M+	227	189.01	193.10	190.98	242.11	242.11	243.53	239.00	242.93	243.29	227.29	228.09	231.67
Ph<->OC-C6H4-NO2+	77 + 150	309.95	293.82	282.74	357.77	328.90	353.09	347.99	344.31	344.36	312.79	335.27	333.51
Ph-OC-<->C6H4-NO2+	105 + 122	257.60	269.42	259.09	329.93	330.70	330.46	324.21	328.43	328.06	304.43	306.77	308.15
O2N-C6H4-CO+	150	130.39	149.25	149.56	210.31	209.33	210.64	203.21	205.82	207.73	186.33	187.14	189.70

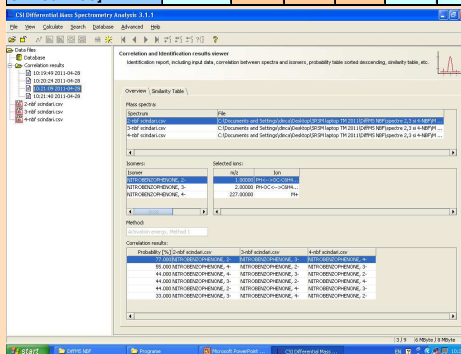


Figure 1. The probability window shows the input of similar mass spectra of position aromatic isomers, 2-, 3- and 4- nbf, the selection of quantum chemical data for the possible isomers and the percentage of structures assignment.

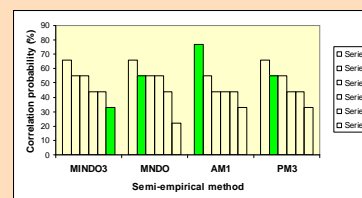


Figure 2. Probability series of structures assignment. The correct assignment has a green format.

d) Taking into account the research methodology, the probability of settlement of the structures of the three etalons becomes a quality indicator of the formation heats used from the database. This way, the best quantum chemical method in this case is AM1 because its correct assignment probability is the highest.

## DISCUSSION

✓ 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 analysed structures from calculation data.

### Acknowledgements

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