MASS SPECTROSCOPIC STUDY OF BIS-CARBAMATE MEE-1 BY *IN SILICO* METHOD

Eldor Mashaev
Senior lecturer of the Tashkent Institute of Chemical Technology
Abduhamid Makhsumov
Professor of the Tashkent Institute of Chemical Technology
Umidjon Beshimov
Employee of the plant GTL Uzbekistan

Abstract. In organic chemistry, mass spectrometry (MS) is the method most often used to identify and study the structures of substances. Because this typically involves matching a given MS spectrum to an experimentally derived reference spectral library, this approach is limited by the coverage and size of such libraries. These experimental libraries can be greatly expanded by predicting MS spectra of unknown chemical structures to create computational reference spectral libraries. In this research work, the bis-carbamate we synthesized was calculated in these libraries and will serve in the future for comparison with data obtained from the MS spectrometer.

Key words: Bis-carbamate, structure, identify, spectrum, databases, in silico, ionization, electrospray, fragmentation, peaks.

Introduction. Carbamates, or urethanes, are derivatives of carbamic acid (carbonic acid amide), the amino and carboxyl ends of which are replaced by a variety of structurally diverse alkyl, aryl or alkylaryl substituents and are identified by the presence of an R-O-CO-NH-R bond [1]. They are used in crops and in everyday life to kill cockroaches, ants, fleas, crickets, aphids, scale insects, whiteflies, lace bugs and mealybugs. Some carbamates control mosquitoes. Some carbamates have been detected in groundwater in quantities high enough to be of concern [2]. The authors of this article synthesized bis-carbamates of the MEE series. The mechanism and parameters influencing the reaction have been studied [4-7,17]. The resulting product was studied in international chemical databases and classified according to the product range of foreign economic activity of the Republic of Uzbekistan [10,18]. Also, they were studied by spectral analysis methods and examined for acute toxicity [8,9,11,15,16,19]. Used as a plant biostimulator and corrosion inhibitor for metals and fuels [12-14]. The purpose of this work is to *in silico* study the mass spectra of N,N′-hexamethylene bis-[(o-cresolyl)-carbamate] i.e. MEE-1. The CFM-ID 4.0 web server (https://cfmid.wishartlab.com) is an online tool for predicting, annotating and interpreting tandem mass (MS/MS) spectra of small molecules. It is specifically designed to assist researchers pursuing studies in metabolomics, exposomics and analytical chemistry. More specifically, CFM-ID 4.0 supports the: 1) prediction of

electrospray ionization quadrupole time-of-flight tandem mass spectra (ESI-QTOF-MS/MS) for small molecules over multiple collision energies (10 eV, 20 eV, and 40 eV); 2) annotation of ESI-QTOF-MS/MS spectra given the structure of the compound; and 3) identification of a small molecule that generated a given ESI-QTOF-MS/MS spectrum at one or more collision energies. The CFM-ID 4.0 web server makes use of a substantially improved MS fragmentation algorithm, a much larger database of experimental and in silico predicted MS/MS spectra and improved scoring methods to offer more accurate MS/MS spectral prediction and MS/MS-based compound identification [3].

Materials and Methods. We use web server CFM-ID 4.0 with function predicts QToF MS/MS spectra for multiple collision energies for a given input small molecule. Spectra are computed for low (10 eV), medium (20 eV) and high (40 eV) collision energy levels and are represented by a list of 'mass intensity' pairs, each corresponding to a peak in the spectrum.

Results and Discussions. Spectrum Prediction Input Parameters:

Parent Compound Structure (SMILES Format)	c1cc(c(cc1)OC(=O)NCCCCCCNC(=O)Oc1ccccc1C)C
Parent Compound Mass	384.20490738579997
Spectra Type	ESI
Ion Mode	Positive
Adduct Type	[M+H]+
Probability Threshold	0.001
Status	**Completed**

Predicted spectra are shown below. Peaks for which corresponding fragments have been found are colored red; unassigned peaks are colored blue. A list of all possible matching fragments is shown below the spectra Fig. 1-4.

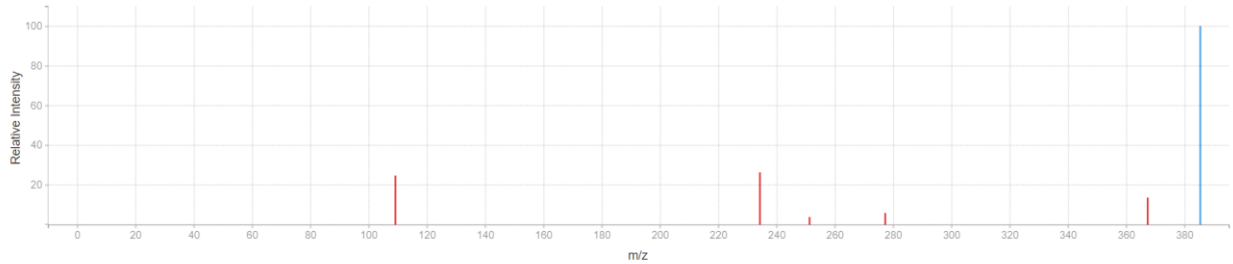


Fig. 1. Predicted Low Energy MsMs Spectrum (10V), [M+H]+

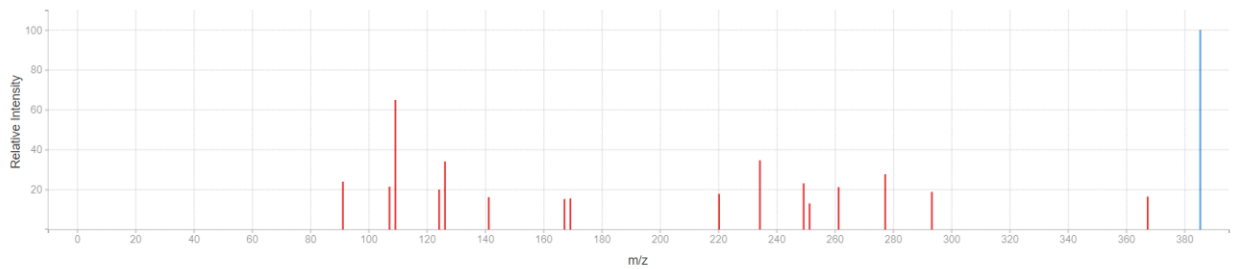


Fig. 2. Predicted Medium Energy MsMs Spectrum (20V), [M+H]+

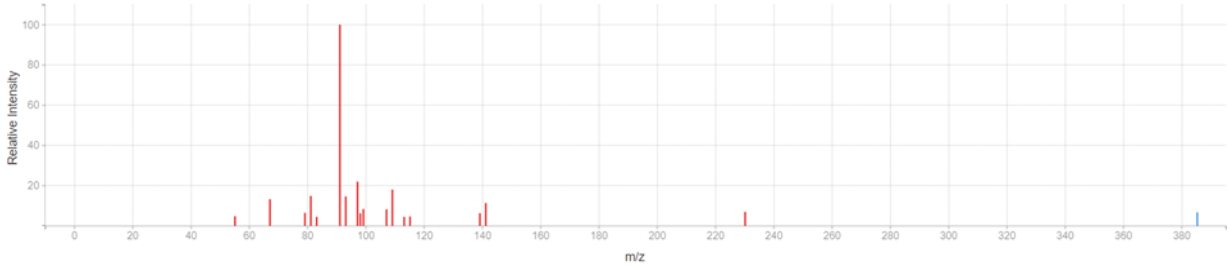


Fig. 3. Predicted High Energy MsMs Spectrum (40V), [M+H]+

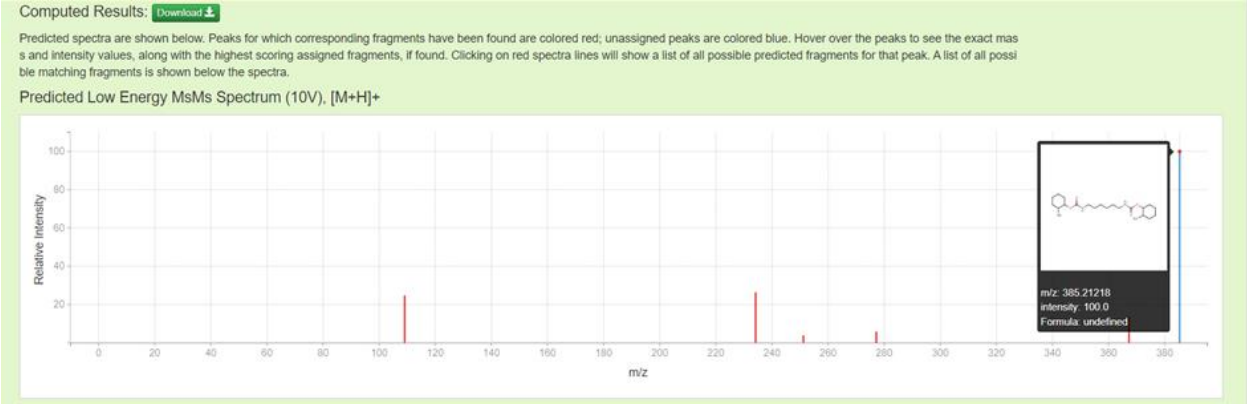


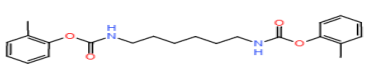
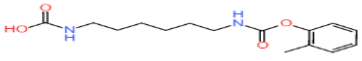
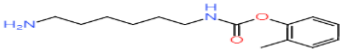
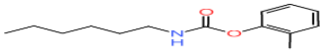
Fig. 4. MsMs Spectrum of bis-carbamate MEE-1 in (10V), [M+H]+

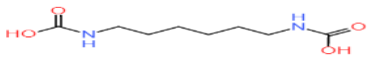
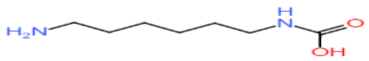
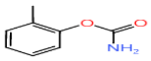
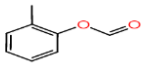
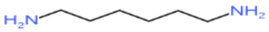
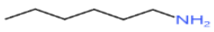
Spectra Peaks and Possible Matching Fragments for c1cc(c(cc1)OC(=O)NCCCCCCNC(=O)Oc1ccccc1C)C: energy0 - 109.06479, 234.14886, 251.1754, 277.15467, 367.20162, 385.21218; energy1 - 91.05423, 107.04914, 109.06479, 124.07569, 126.09134, 141.10224, 167.0815, 169.09715, 220.13321, 234.14886, 249.15975, 251.1754, 261.15975, 277.15467, 293.14958, 367.20162, 385.21218; energy2 - 55.05423, 67.05423, 79.05423, 81.06988, 83.08553, 91.05423, 93.06988, 97.10118, 98.09643, 99.11683, 107.04914, 109.06479, 113.10732, 115.12297, 139.08659, 141.10224, 230.11756, 385.21218.

After obtaining spectral data, we built a table of fragments of the MEE-1 molecule, Table 1.

Table 1

Fragments of the bis-carbamate MEE-1

Structure	Formula	Mol mass	m/z
	$C_{22}H_{28}N_2O_4$	384.47	385.2122
	$C_{15}H_{22}N_2O_4$	294.35	295.1652
	$C_{14}H_{22}N_2O_2$	250.34	251.1754
	$C_{14}H_{21}NO_2$	235.32	236.1645

	$C_8H_{16}N_2O_4$	204.22	205.1183
	$C_7H_{16}N_2O_2$	160.21	161.1285
	$C_8H_9NO_2$	151.16	152.0706
	$C_8H_8O_2$	136.15	137.0597
	$C_6H_{16}N_2$	116.20	117.1386
	$C_6H_{15}N$	101.19	102.1277
	C_7H_8	92.14	93.0699
	C_6H_6	78.11	79.0542
	CH_3NO_2	61.04	62.0237
	CO_2	44.01	44.9971
	$CH_3(-)$	15.03	16

Conclusion. In conclusion, it should be noted that the CFM-ID 4.0 web server offers a set of utilities to simplify automated MS/MS spectral prediction, spectral annotation and chemical compound identification. Thus, the bis-carbamate we studied was identified and divided into fragments that indicate the structure of the substance. The data we obtained will help us compare the reference spectra with the analyzed one.

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