STUDY OF THE STRUCTURE OF BIS-CARBAMATES OF THE MEE SERIES USING NMR AND MASS SPECTRAL ANALYSIS METHODS

[1]Eldor Mashaev, [2]Abduhamid Makhsumov, [3]Bahodir Fakhriddinov, [4]Askar Parmanov
[1]Senior lecturer of the Tashkent Institute of Chemical Technology
[2]Professor of the Tashkent Institute of Chemical Technology
[3]Professor of the Navoi State Mining and Technology University
[4]Associate professor of the National university of Uzbekistan
https://doi.org/10.5281/zenodo.10360683

Abstract. *In this work, the structure and structure of bis-carbamate of the MEE series were studied using NMR and mass spectroscopy. As a result, the proton and carbon signals of the bis-carbamate molecule were identified and the structure was constructed. By ionization of the molecule, fragments of the molecule were studied and the composition was proven. The identified spectra correspond to the structure and composition of the MEE molecule.*
Keywords: *bis-carbamate, structure, molecule, composition, ionization, NMR, mass spectroscopy, proton, carbon, spectrometer.*

Introduction. Synthesis of biologically active compounds in organic synthesis, their successful use of bis-carbamates in the production of various chemicals, inhibitors, fillers, additives, biostimulants, herbicides, drugs against diseases in the chemical industry, agriculture and pharmaceuticals in the modern world is one of the important issues. Therefore, in this regard, it is of particular importance to create cheap, high-efficiency, environmentally friendly, energy-efficient synthesis methods and to study their physico-chemical and biological properties [1-3].

Researchers have synthesized bis-carbamates and their derivatives and applied them as metal corrosion inhibitors and biostimulants for plant growth [4,5]. The authors of this article also synthesized N, N- hexamethylene bis-[(ortho-cresolyl)-carbamate] i.e. MEE-1 and its derivatives on the basis of hexamethylene diisocyanate and cresols, studied their physico-chemical, biological properties and applied them in various fields has arrived [6-9]. This research work is devoted to studying the structure and composition of MEE-1 bis-carbamate molecule by NMR and mass spectroscopic methods.

Materials and Methods. The substance under study is N,N- hexamethylene bis-[(ortho-cresolyl)-carbamate] i.e. MEE-1. ^{1}H and ^{13}C NMR spectra of MEE-1 substance Pyridine-d5 isotope (C_5H_5N) was obtained on the JNM-ECZ400R spectrometer of Japan (JEOL) with an operating frequency of 400 MHz for ^{1}H at the Institute of Chemistry of Plant Substances named Acad. S.Yu. Yunusov Academy of Sciences of the Republic of Uzbekistan. Mass spectra of MEE-1 were obtained on an Agilent Technologies 6420 spectrometer in a 5% phenylmethylsilicon liquid phase. We used the ISIC-EPFL mass spectrometry platform to divide the ions into fragments and determine the Brutto formulas. The same HPLC data was obtained by the chemical ionization method in high-performance liquid chromatography-MS (HPLC-MS).

Results and Discussions. In the ^{1}H-NMR-spectrum of MEE-1 compound (Fig. 1) 1.407 ppm in the field, the pentite signal of four protons in the methylene group in the 3,4 position of hexane, the triplet-triplet signal of the four protons in the methylene group in the 2,5 position is 1.668 ppm, and the triplet signal of the methylene group in the 1.6 position is 3.440 ppm appeared in the fields. The doublet-doublet-doublet signal of proton atoms located in the 3,4 position of the aromatic ring is 7.126-7.216 ppm fields, and the multiplet signals of proton atoms located in the

5.6 state of the molecule are 7.38-7.58 ppm observed in the fields. The singlet signals of protons of the methyl group located in the aromatic ring is 2.301 ppm observed in the field.

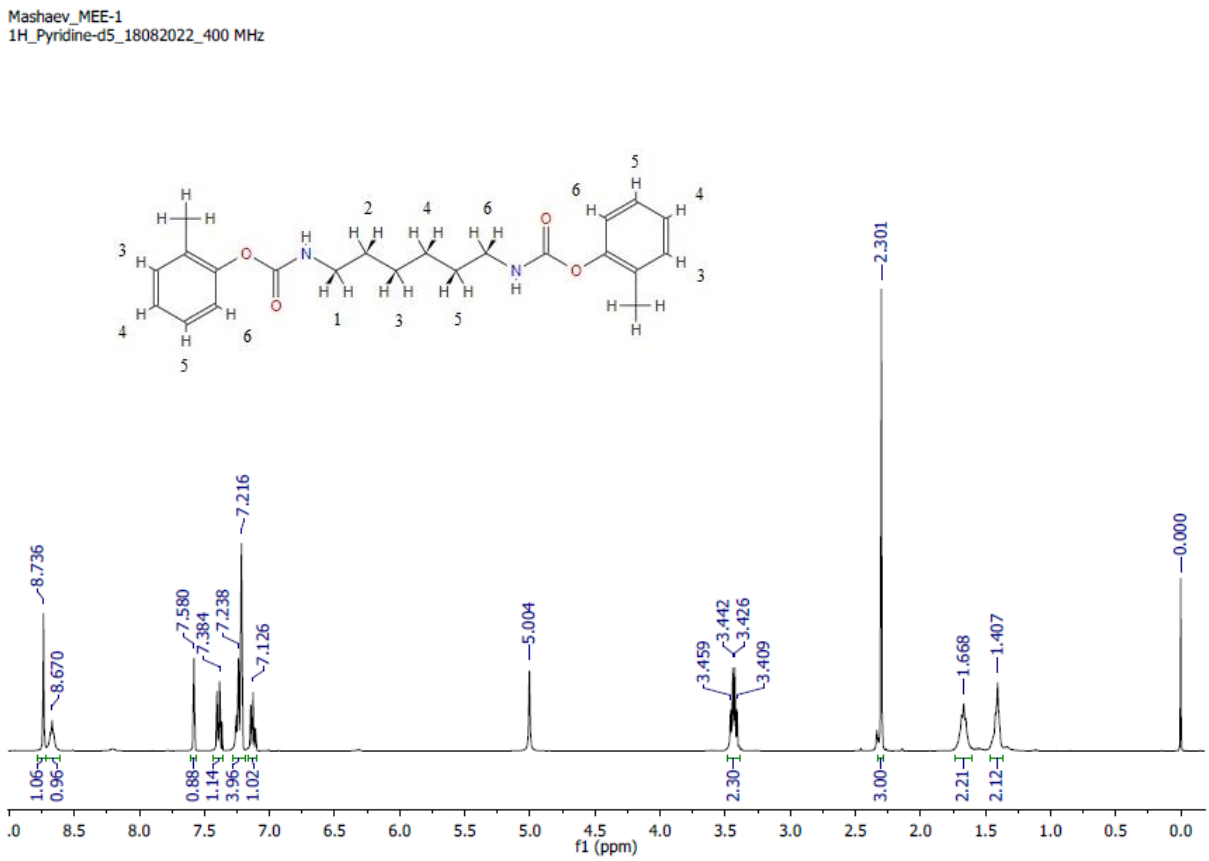

Fig.1. ^{1}H-NMR spectrum of compound MEE-1

In the ^{13}C spectrum of the MEE-1 compound (Fig. 2), the signal of the carbon atom of the carboxyl group of carbamate acid is 151,369 ppm in the sphere, the signal of carbon atoms in the 3,4 and 2,5 states of the hexane chain is 27,281-30,751 ppm fields, and the signal of carbon atoms in the 1,6 state is 41.904 ppm observed in the fields. The signal of the carbon atom in the 1st position of the aromatic ring with oxygen is 156 ppm in the field, the signal of carbon atoms in the 2-5 position is 123.65-131.758 ppm observed in the fields. The absorption signal of the carbon atom in the methyl group is 16.723 ppm observed in the field.

N, N- hexamethylene bis-[(ortho-crezolilo)-carbamate]. *^{1}H_NMR: δ 1.4 (4H, quint, J = 7.0 Hz), 1.67 (4H, tt, J = 7.1, 7.0 Hz), 2.3 (6H, s), 3.44 (4H, t, J = 7.1 Hz), 7.126 (2H, ddd, J = 8.1, 7.5, 1.5 Hz), 7.21-7.38 (4H, 7.21 (ddd, J = 8.2, 1.5, 0.5 Hz), 7.38 (ddd, J = 8.2, 7.5, 1.2 Hz)). 13C NMR: δ 16.0 (2C, s), 27.1 (2C, s), 29.4 (2C, s), 40.6 (2C, s), 115.8 (2C, s), 126.1 (2C, s), 128.4 (2C, s), 128.9 (2C, s), 129.4 (2C, s), 154.3 (2C, s), 156.3 (2C, s).*

When determining the mass spectra of bis-carbamates, we used high-resolution mass spectra, because in low-resolution mass spectra, the m/z ratio is rounded to whole numbers, so ions with similar masses in the spectrum are recorded as one peak. In high-resolution spectra, the mass of ions is determined to the fifth or sixth decimal place, for example: *m/z*(CO)=27.994915 (Fig. 3).

The Retro-Diels-Alder (RDA) reaction mechanism is an important pathway for the cleavage of the C-bond of bis-carbamates. As a result of RDA degradation, three characteristic fragments appear, which provide useful information about the number of aromatic rings, methyl groups and other substituents in the molecule.

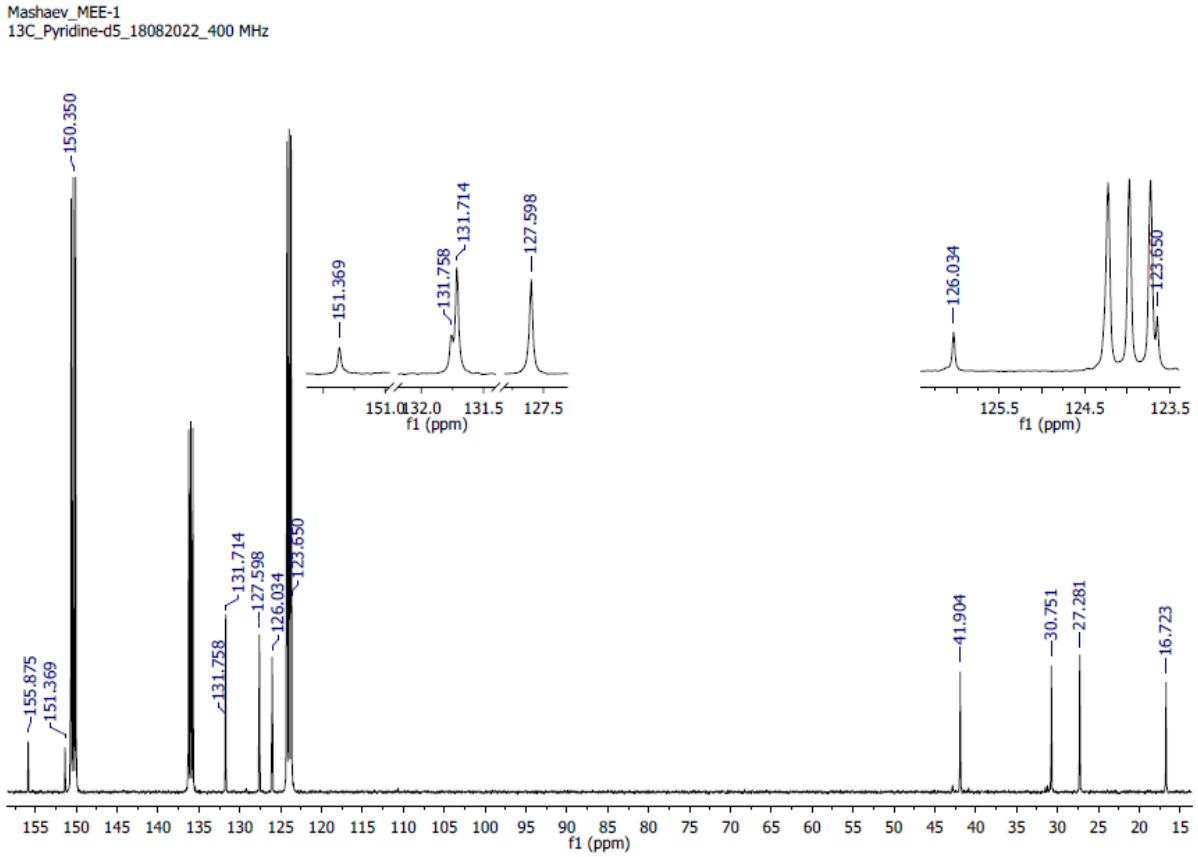

Fig. 2. ^{13}C-NMR spectrum of compound MEE-1

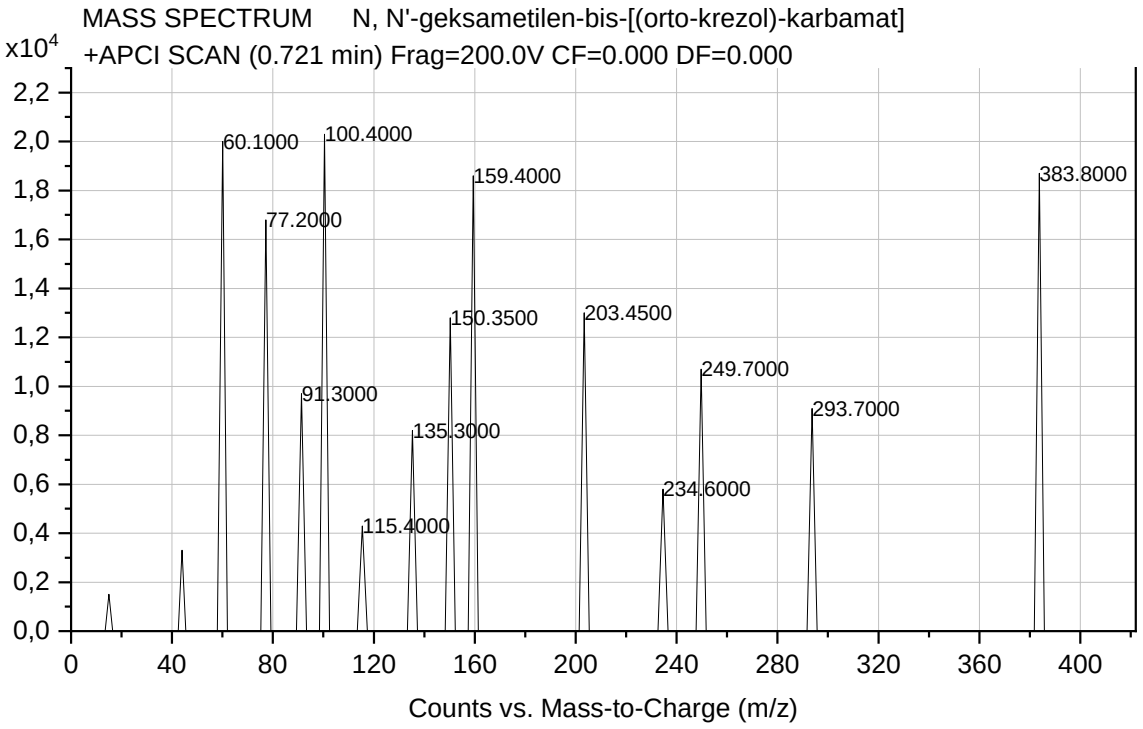

Fig. 3. Mass spectrum of compound MEE-1

The same HPLC data was obtained by the chemical ionization method in high-performance liquid chromatography-MS (HPLC-MS). During the electronic ionization of bis-carbamates, the splitting of the $[M-H]^+$ ion begins with the breaking of the aromatic ring in the ortho position. This leads to the formation of the highly stable methylbenzene anion, and this type of decomposition is known as the approach effect. The cation thus formed is rearranged, followed by decomposition, which ultimately leads to the loss of CO_2.

In Figure 3.2.7.1, the total molecular peak of MEE-1 was equal to m/z 383 at 1.9 intensity at 0.513 min. Above we said that fragmentation occurred in three directions, in which in the first direction m/z 249 at 1.1 intensity at 0.196 min, m/z 135 at 0.8 intensity, m/z 91 at 1.0 intensity, cation fragments, second m/z 234 at 0.6 intensity in direction 0.189 min, m/z 100 at 2.0 intensity and m/z 293 at 0.9 intensity in 0.187 min in the third direction, m/z 202 at 1.3 intensity, m/z 249 at 1.1 intensity, Fragment cations with m/z 114 at 0.4 intensity, m/z 158 at 1.9 intensity, and m/z 59 at 2.0 intensity were formed.

Conclusion. The above-mentioned signals and spectra made it possible to establish the structure and composition of MEE-1 bis-carbamate. This proves that the synthesized substance was created and our scientific work was carried out effectively. But we think that these studies are not enough and we believe that they should be continued.

REFERENCES

1. Makhsumov A.G., Ismatov D.N., Valeeva N.G., Asadova R.D., Ruzmatov B. Modern advences in the synthesis of new derivatives of acetylene dithiocarbamate and their biological activaty // “Internathional journal of Engineering and Scientific Research, 2019, vol.7, Issue 3, March (India), pp.1-9.
2. Sutoris V., Sunak J., Cipinova H. Preparation of ethinyl esters and carbamates and the study of their pesticidal action // Chem.J.Vesti, 23, № 11, 1969, P.47-48.
3. Khatamova M.S., Makhsumov A.G. Moderm achievements in the synthesis of bis (alkyl) - carbamate derivatives and their propirties // Chemical Journal of Kazakhstan, Special issue - Almaty, 2007, R. 120-124.
4. Абдурахманов У.К., Холбоев Ю.Х., Юсупов М.М., Махсумов А.Г. Синтез биостимулятора на основе производных бискарбамата // Universum: химия и биология. 2019. №12 (66). с. 31-33.
5. Махсумов А.Г., Холикулов Б.Н., Холикова С.Д. Синтез супербиостимулятора на основе производных бис-[(4-бромфенокси) -карбамата], свойства и применение // Universum: химия и биология : электрон. научн. журн. 2020. № 10(76). с. 151.
6. Махсумов Абдухамид Гафурович, Абдукаримова Саида Абдужалиловна, Машаев Элдор Эргашвой Угли, and Азаматов Уткирбек Рашидович. "Синтез и свойства производного - N,N' quote -гексаметилен бис - [(орто-крезолило) -карбамата] и его применение" Universum: химия и биология, no. 10-2 (76), 2020, pp. 33-40.
7. Махсумов А.Г., Жагфаров Ф.Г., Арипджанов О.Ю., Машаев Э.Э., Азаматов У.Р. "Синтез и свойства производных мета-крезолило-карбаматов, их биологическая активность" НефтеГазоХимия, №3, 2022, 52-59 с. doi:10.24412/2310-8266-2022-3-52-59
8. Махсумов Абдухамид Гафурович, Машаев Элдор Эргашвой Угли, Холбоев Юсубжон Хакимович, Уразов Фируз Бахтиярович, and Зохиджонов Сирожиддин Аскаржон Угли. "N,N’–гексаметилен бис [(м-крезолило) -карбамат] и его физико-химические свойства" Life Sciences and Agriculture, no. 1 (9), 2022, pp. 7-11.
9. Mashayev, E., Ismailov, B., Ergashev, J., Omonov, S., & Makhsumov, A. (2023). Research of N,N′-hexamethylene bis-[(o-cresolyl)-carbamate] in international chemicals databases. B

International Bulletin of Applied Science and Technology (Т. 3, Выпуск 11, сс. 397–401). Zenodo. https://doi.org/10.5281/zenodo.10209951