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STUDYING THE STRUCTURE OF BIS-CARBAMATE OF THE MEE SERIES BY IR SPECTRAL ANALYSIS METHOD

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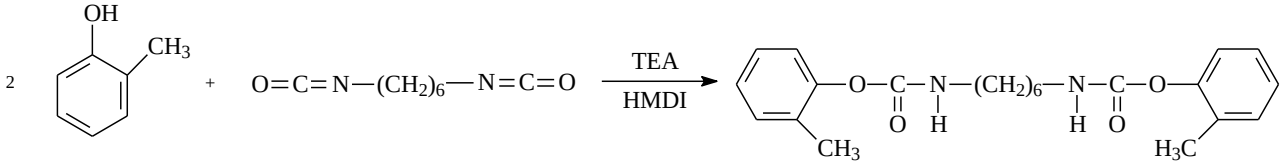
Abstract. *In this research work, the IR spectra of the reagent molecules that react to synthesize N, N'-hexamethylene-bis-[(o-cresol)-carbamate] i.e., MEE-1 were studied by the attenuated total internal reflection method. The length and strength of bonds between bis-carbamate atoms were studied and calculated using the quantum chemical method. During the work, the similarities between the spectra of bis-carbamate and other substances were studied using international databases. As a result, absorption spectra of functional groups such as amine, methyl, carbonyl, aromatic, and ether, characteristic of carbamate groups, were identified, which proves the structure of bis-carbamate MEE-1.*

Keywords: *bis-carbamate, cresol, hexamethylene diisocyanate, vibrations, spectrum, bond, quantum, molecule, atom, structure.*

Introduction. Esters of carbamic acids - urethane and carbamate compounds with the general formula R'R"NCOOR are widely used in various industries. Representatives of this class of chemical compounds exhibit broad biological activity, due to which they are used as additives, medicines (for example, proserin and carbacholin) and plant protection products (herbicides, fungicides, insecticides, acaricides and plant growth stimulants) [1]. In recent years, increased interest in bis-carbamate compounds is associated with the possibility of use in a variety of fields. Polyurethanes are widely used in industry, used in the form of urethane rubbers, polyurethane adhesives, varnishes, and fibers [2,3].

The authors of this article synthesized about twenty bis-carbamate compounds and used them as a metal corrosion inhibitor, a fuel antioxidant, and a plant biostimulator [4-6]. Despite the low toxicity of these compounds for the human body, some of them are very important for stimulating growth and protecting against crop pests [7-9]. The purpose of this work is to study the structure of the synthesized N,N'-hexamethylene-bis-[(o-cresol)-carbamate], i.e. MEE-1 and reaction reagents using IR spectroscopy combined with quantum calculations. The synthesis of bis-carbamate MEE-1 was carried out by the method described in the literature [10-13]. Scheme for the synthesis of bis-carbamate MEE-1:



The nitrogen and oxygen atoms in the –N=C=O group of hexamethylene diisocyanate (HMDI) are primarily negatively charged and electron-donating, making this group susceptible to both nucleophilic and electrophilic attacks. In some cases, diisocyanates can also act as

electrophilic agents. The most typical reactions for them are nucleophilic addition reactions involving oxygen and nitrogen-containing substances.

Materials and Methods. Preparation of N,N'-hexamethylene bis-[(o-cresol)-carbamate]: Add to 8.40 g (0.1 mol) ortho-cresol, 10 ml of triethylamine, 35 ml of DMF, add dropwise with stirring at room temperature 8.42 ml (0.05 mol) hexamethylene diisocyanate dissolved in 20 ml of DMF.

The reaction mixture is stirred for 3.0-4.0 hours at a temperature of 35-45 °C; after the time has elapsed, the contents of the flask are transferred to a glass and water is added. The resulting precipitate is washed with TLC.

After drying, a snow-white powder is obtained, the product yield is 18.74 g (97.6% of theoretical). IR spectra of bis-carbamate MEE-1 were recorded on a Nicolet iS50 spectrometer (Th. scientific, USA) using the ATR method at the Center of Advanced Technologies under the Ministry of Innovation of the Republic of Uzbekistan. Similarities were examined using the HR Nicolet Sampler Library, HR Aldrich Hydrocarbons and Aldrich Vapor Phase Sample Library databases. To create a three-dimensional structure and study the strength and bond lengths of the MEE-1 molecule, the Gaussian 09 program and the M06-2X hybrid functional calculation method were used [14,15].

Results and Discussions. During the IR spectral analysis of the MEE-1 molecule, quantum chemical calculations were also carried out. The reason is that the types, lengths and strengths of bonds are very important when studying the IR spectra of a molecule. Figures 1 and 2 show the structural formula and three-dimensional view of the MEE-1 molecule with calculations of the bond lengths of the atoms:

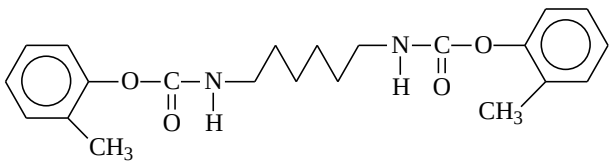


Fig. 1. Structural formula MEE-1

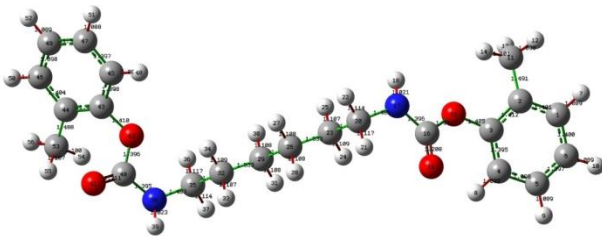


Fig. 2. Bond lengths of the MEE-1 molecule

In Figure 2, the bond lengths of the MEE-1 molecule are calculated, where the length of the double bond C1=C6 in the aromatic ring is 1.40 Å, the length of the C1-H7 bond is 1.08 Å, the length of the C2-C11 bond associated with the methyl radical of the ring is 1.49 Å, the C3-O15 bond length is 1.40 Å. The O15-C16 bond length of the ester group is 1.40 Å.

The length of the double bond of the carbonyl group C16=O19 is 1.20 Å, the length of the bond of the carbon atom C16-N17 of the carbonyl group is 1.39 Å.

The length of the N17-H18 bond of the amino group is 1.02 Å, the length of the bond of the N17-C20 nitrogen atom of the amino group is 1.48 Å. The C20-C23 bond length in hexamethylene is 1.53 Å, and the C20-H21 bond length in hexamethylene is 1.11 Å. Since the reaction center in the MEE-1 molecule is the amino group, it should be noted that the length of the N17-H18 bond is 1.02 Å, and the breaking energy is 93 kcal/mol.

Afterwards, the spectra of the reagents hexamethylene diisocyanate and ortho-cresol reacting for the synthesis of MEE-1 were studied, Figures 3 and 4:

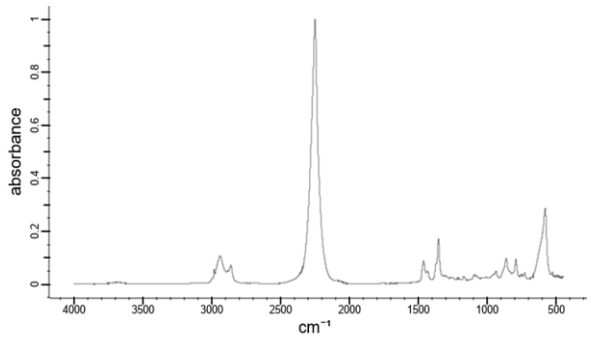


Fig. 3. IR spectrum of hexamethylene diisocyanate

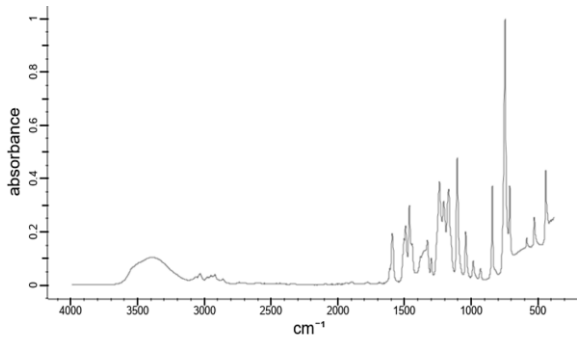


Fig. 4. IR spectrum of ortho-cresol

The IR spectrum of HMDI (Fig. 3) contains a high-intensity band at 2270 cm^{-1} and a band at 1350 cm^{-1}, corresponding to asymmetric and symmetric vibrations of the –N=C=O bond. Absorption bands of CH_2 groups are also observed, corresponding to asymmetric and symmetric vibrations in the frequency ranges of 2950 cm^{-1} and 2850 cm^{-1}. In the IR spectrum of ortho-cresol (Fig. 4.), the presence of an OH group is confirmed by characteristic bands in the frequency range of 3400 cm^{-1} and 3200 cm^{-1}; in the frequency range above 3000 cm^{-1} there is a peak corresponding to C–H bonds in aromatic ring. Stretching vibrations of the C=C bonds of the benzene ring are characterized by bands at 1620, 1350 cm^{-1}. The presence of an intense band at 1470 cm^{-1} and a low intensity absorption band of the benzene ring at 1500 cm^{-1} is characteristic of cresols with ortho substituents. The presence of a methyl group in this compound is confirmed by bands of symmetrical bending vibrations in the frequency range of 1310 cm^{-1}.

Afterwards, we carried out a similarity analysis of the IR spectrum of the MEE-1 compound using library databases. Figure 5 shows "Lorazepam" with a similarity of 21.59%, this corresponds to the aromatic ring, amine group and carbonyl group of the bis-carbamate. “Polyurethane resin” with a similarity of 19.78%, that is, a compound containing several urethane (carbamate) –N(R)-(CO)O- groups. Also, “Polycarbonate, bisphenol A” with a similarity of 18.53% indicates the presence of several phenolic and carbonyl Ar-O-CO bonds as well as in the bis-carbamate molecule. In Figure 6, “2,2’-dimethylbibenzyl” was identified with a similarity of 26.42%, which suggests the presence of an aromatic ring and an amine group. “4-phenyltoluene” with a similarity of 25.30% indicates the presence of methyl in the aromatic ring. Also, with a similarity of 21.98%, “1,6-diiodohexane” is represented, this indicates the presence of hexane in the bis-carbamate molecule. The presence of “Verbenone” and “Isophorone” with similarities of 28.60% and 20.51% in Figure 7 indicates that MEE-1 molecule has a carbonyl group and a methyl group in the aromatic ring. You can also see "4-propylphenol" with a similarity of 26.53%, which corresponds to the presence of an H_3C-Ar-O- bond in the bis-carbamate molecule. And also, “Pyrazol” with a similarity of 20.74% indicates the presence of the amine group of MEE-1. In Figure 8, the similarity of the peaks was checked and the peaks of “Aliphatic acetate esters” were identified, indicating the presence of a carbonyl C=O and C-O-C ester group in the bis-carbamate molecule. Also, the peaks of “Aliphatic secondary amines” prove the presence of an N-H amine group in the bis-carbamate molecule.

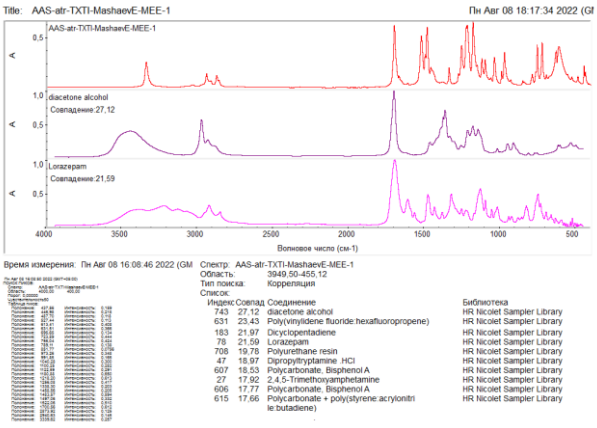


Fig. 5. MEE-1 similarity spectra in the HR Nicolet Sampler Library

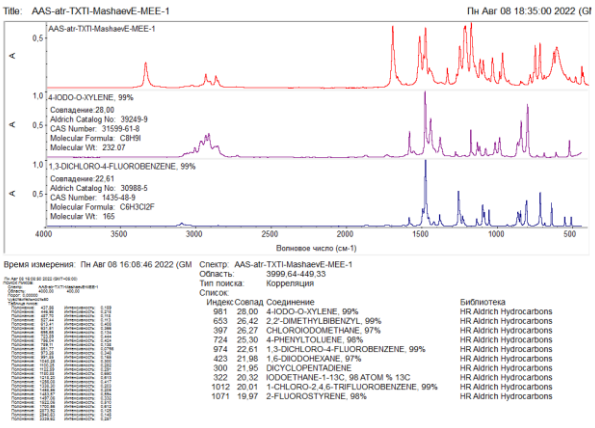


Fig. 6. Similarity spectra of MEE-1 in the HR Aldrich Hydrocarbons library

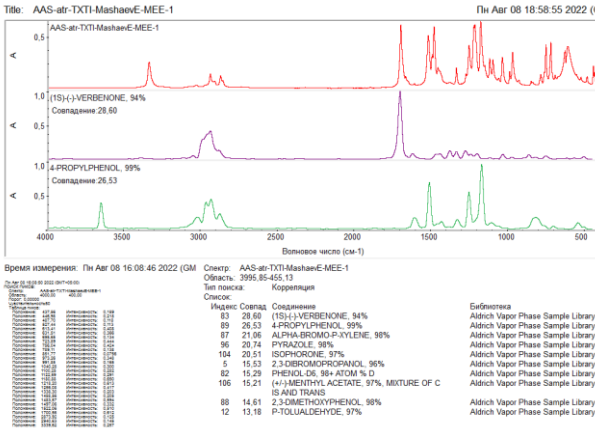


Fig. 7. Similarity spectra of MEE-1 in the Aldrich Vapor Phase Sample Library

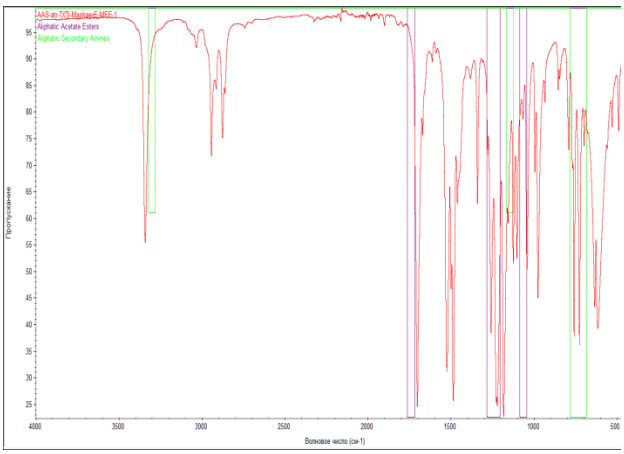


Fig. 8. Comparison of similarity peaks of bis-carbamate MEE-1

But given that the accuracy of these comparisons is very low, we separately analyzed the spectrum of bis-carbamate MEE-1 (Fig. 9).

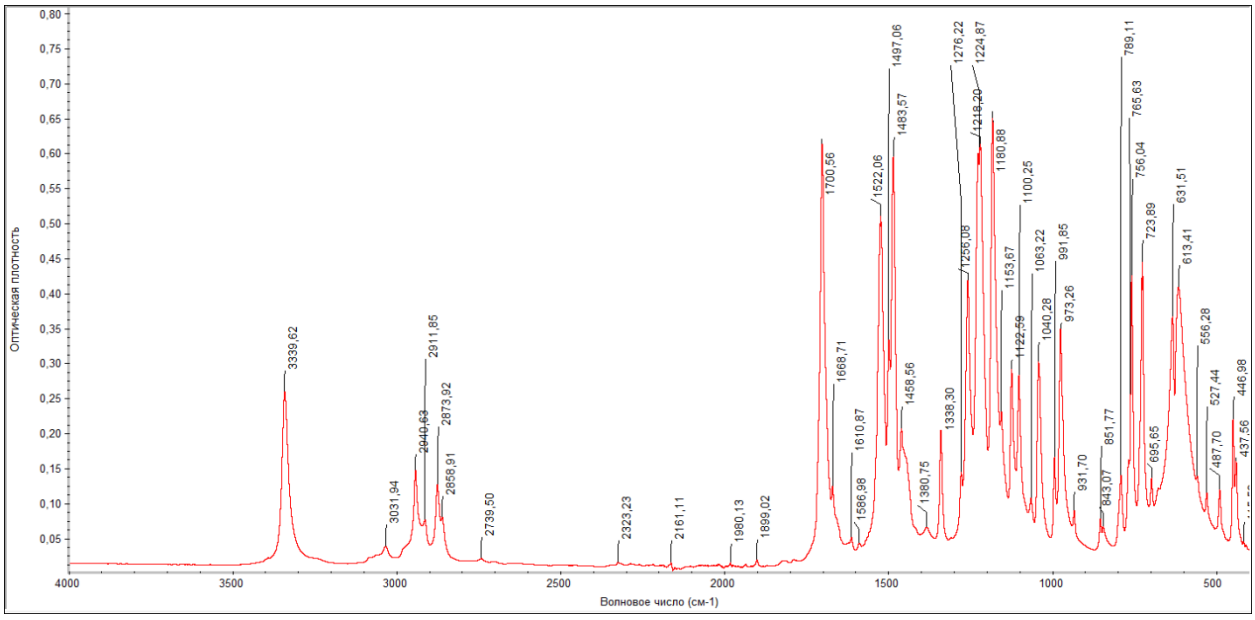


Fig. 9. IR spectrum of N, N'-hexamethylene-bis-[(o-cresol)-carbamate] i.e., MEE-1

In the IR spectrum of bis-carbamate MEE-1 (Fig. 9.), the disappearance of absorption bands corresponding to the –N=C=O groups of isocyanate (ν = 2270 cm^{-1}) is observed. The spectrum shows vibrations characteristic of carbamate groups N-(CO)-O– in the frequency range of 1224.87 cm^{-1}. The ring vibration of the aromatic ring appeared in the frequency range of 1483 cm^{-1}, the average stretching vibration characteristic of the C-N bond was in the frequency range of 3032 cm^{-1}, and the bending vibration appeared in the frequency range of 631 cm^{-1}. A highly asymmetric stretching vibration of the methyl group (CH_3) on the aromatic ring was observed around 2940.63 cm^{-1}. The methylene groups of o-cresol carbamate (-CH_2) have a high asymmetric stretching vibration in the frequency range of 2941 cm^{-1}, a symmetric stretching vibration in the frequency range of 2858 cm^{-1}, and a weak sharp bending stretching vibration in the frequency range of 1458 cm^{-1}. In the spectra, spindle and pendulum vibrations were observed, respectively, in the frequency range of 1338.30 and 723.89 cm^{-1} of the methylene groups. High stretching vibrations to the amino group (NH) were observed in the frequency range of 3340 cm^{-1}, and stretching vibrations characteristic of the -C-N bond were observed in the frequency range of 1181 cm^{-1}. Intense absorption lines of the carbonyl group (C=O) were observed in the frequency range of 1700 cm^{-1}. Very strong stretching vibrations of the ether bond (C-O-C) in intensity were observed in the absorption frequency range of 1256 cm^{-1}.

Conclusion. Using IR spectroscopy, it was established that comparison of the spectra of bis-carbamate MEE-1 in international electronic library databases did not give the desired result. However, there were several coincidences confirming the presence of urethane (carbamate) –N(R)-(CO)O- groups, as well as bonds such as Ar-O-CO-, H_3C-Ar-O- in the MEE-1 molecule. To analyze the vibration frequencies, various manuals intended for the interpretation of IR spectra were used, and the vibrations of the molecule were determined from the results of the spectrum. Thus, the results obtained allow us to conclude that the presence of spectra of the methyl group (CH_3), carbonyl group (C=O), amino group (NH) and absorption bands characteristic of carbamate N-(CO)-O– groups in the frequency range 1224 cm^{-1} proves that the synthesized substance is precisely N,N'-hexamethylene-bis-[(o-cresol)-carbamate], i.e. MEE-1.

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