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 TECHNOLOGY**
**SYNTHESIS, PROPERTIES AND BIOLOGICAL ACTIVITY N, N¹ -
 HEXAMETHYLENE [BIS-(1-NAPHTHOXY) -CARBAMATE]**
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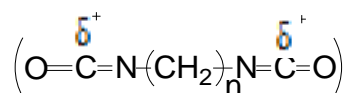
ABSTRACT

The chemical properties of N, N¹-dimethylene bis (naphthoxy) carbamate have been synthesized and studied. Synthesis of bis-carbamate derivatives is carried out. N, N¹-dimetallation, alkylation, chlorination, nitrosation, the biostimulating properties of the compounds obtained.

KEYWORDS: hexamethylene, naphthoxy carbamate, chlorination, dimetallation, alkylation, nitrosation

I. INTRODUCTION

As is known, among the derivatives of naphthol carbamates are biologically active compounds that possess bactericidal, fungicidal, pesticidal activity of biostimulators for industrial crops (plants) and many others [1-3]. One of the important sections of organic chemistry and synthesis is that diisocyanate groups have a complex electrophilic-nucleophilic structure with a predominance of electrophilic, due to a large positive charge on the carbon



They are a reaction center in a nucleophilic attachment reaction for non-waste technologies for the production of new environmentally friendly compounds having a wide range of applications.

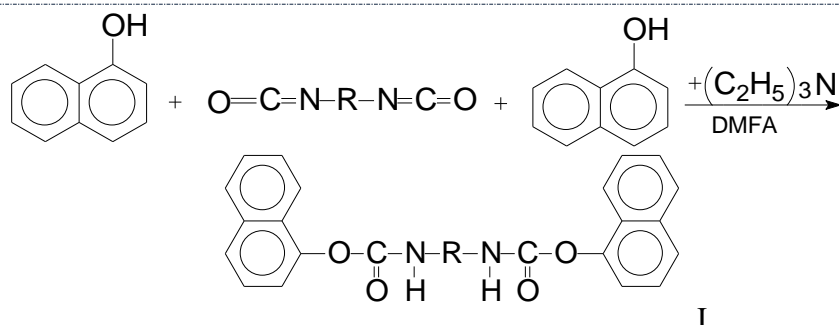
In the world, several dozen drugs are known - derivatives of substituted ureas and carbamates widely used in various sectors of the economy, in agriculture, which determines the relevance of research. From this point of view, the derivatives of naphthol-substituted carbamates and bis-carbamates are of great interest as substances possessing different biological and pharmacological activities. In agriculture, they have found application as pesticides, herbicides, fungicides, insecticides, nematocides, growth stimulators and etc. In medicine, they are used as antiviral, antitumor, anti-inflammatory and other medicinal substances [4-11].

II. MATERIALS AND METHODS

The object of the study were derivatives of naphthol carbamates. Their physical and chemical properties, biostimulating activity were studied. IR spectra recorded on the spectrometer "VR-20" in KBr tablets.

III. RESULTS AND DISCUSSION

We have developed research in the field of the synthesis of new substances. The reaction of naphthol-1 with diisocyanate was carried out and bis (1-naphthoxy) carbamate derivatives were obtained according to the following scheme, where $\text{R} = -(\text{CH}_2)_4-$, $-(\text{CH}_2)_6-$.

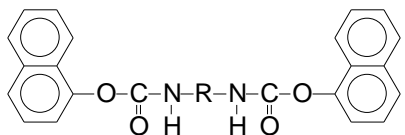


Reactions of diisocyanate with naphthol-1 were carried out at a molar ratio of reactants 1: 2 at a temperature of 26-32 °C, for 35 hours. N, N¹-polymethylene bis [(naphthoxy-1) -carbamate] are formed as a result of the reaction, which are colorless high-melting substances, which are difficult to solubilize in water and other organic solvents, which confirms the presence of two rigid carbamate groups (I).

The structure of the synthesized derivative of O [(naphthoxy-1) -carbamates] was established by IR spectroscopy and confirmed by elemental analysis data (Table 1).

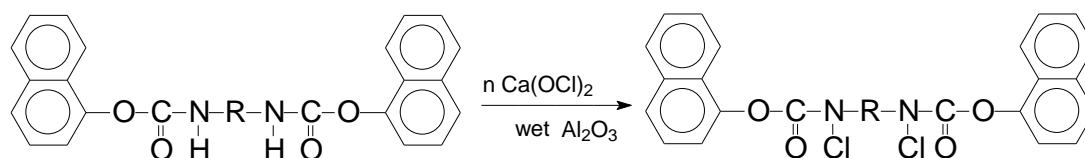
To reveal the reactivity of the N-H groups of naphthoxy-substituted-bis-carbamates, we carried out the following reactions: N, N¹-dichlorination, metallation, alkylation, nitrosation.

Table 1
 Physico-chemical parameters of compound (I)

| Structural formula | Output, % | T _{PL} , °C | R _f | Gross formula C ₂₈ H ₂₆ N ₂ O ₄ | Elemental analysis, % | | IR spectra, cm ⁻¹ | | | M _M |
|---|-----------|----------------------|----------------|--|-----------------------|-------|------------------------------|----------|----------|----------------|
| | | | | | Calculated | Found | -N-C-O- H O | -N- H | -C- O | |
| | | | | | N | N | | | | |
|  | 95,7 | 182-183 | 0,64 | C ₂₈ H ₂₆ N ₂ O ₄ | 6,14 | 6,01 | 1294 | 3330 | 1720 | 456 |

As a result of the reaction of N, N¹-dichlorination of polymethylene bis [(naphthoxy-1) -carbamate derivatives] with calcium hypochlorite on wet alumina for 26 hours in the presence of CHCl₃, compound (II) was obtained (Table 2).

The chemical reaction scheme is the following, where $R = -(CH_2)_6-$.



The structure of the preparation II was determined by the IR spectroscopy and elemental analysis data. In the IR spectrum of the preparation (II), the C=O band exhibits an absorption band in the 1280 cm⁻¹ region, narrow bands in the region of 1718 cm⁻¹ characterize the set of stretching vibrations belonging to the stretching

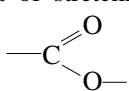


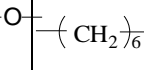
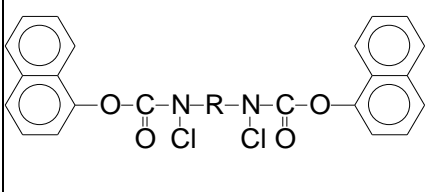
vibrations in the spectra of the bis-carbamate derivative . In addition, the study of the IR spectra of the compound showed that the presence of absorption bands of strong valence vibrations in the 752-720 cm⁻¹ region $-(CH_2)_6-$ indicate the presence of bonds.

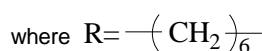
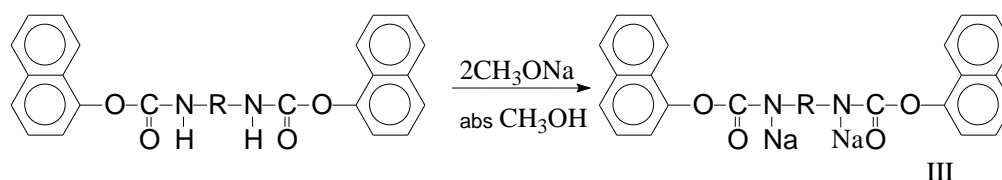
Table 2

Physico-chemical parameters of the preparation (II)

| Structural formula | Output, % | T _{PL} , °C | R _f | Gross formula | Elemental analysis, % | | IR spectra, cm ⁻¹ | | | M _M |
|---|-----------|----------------------|----------------|---|-----------------------|-------|---|---|---|----------------|
| | | | | | Calculated | Found |  |  |  | |
| | | | | | N | N | | | | |
|  | 90,6 | 151-152 | 0,73 | C ₂₈ H ₂₆ Cl ₂ N ₂ O ₄ | 5,33 | 5,19 | 1718 | 1280 | 759-720 | 525 |

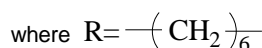
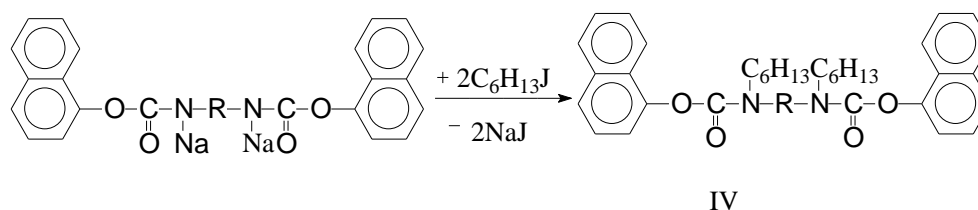
Preparation of N, N¹-disodium substituted polyalkylene bis - [(naphthoxy-1) carbamate] (III)

Naphtho-substituted derivatives of bis-carbamates (I) are subjected to directional N, N¹-dimetallation with N-H groups according to this reaction scheme, by means of with CH₃ONa in abs. methanol, yield (III) is 83,5%.


Preparation of N, N¹-dihexyl substituted derivatives of bis-carbamates (IV)

Hexylation on N-H groups in bis-carbamates (I) by hexyl iodides is of undoubted interest for elucidating the

reactivity $\begin{matrix} \diagup \\ \text{N-Na} \\ \diagdown \end{matrix}$ containing compounds. Hexylation reactions with the interaction of N, N¹-disodium derivatives of N, N¹-polymethylene bis [(naphthoxy-1) -carbamate] with hexyl iodide in dry benzene, at a temperature of 26-31 ° C and stirring, were added dropwise with hexyl iodide over 3,5-4 hours according to the following scheme:



The flow of alkylation reaction exclusively on the nitrogen atom N, N¹- is explained by the relatively easy dissociation of sodium in this atom due to the presence of neighboring carbonyl groups. The yield is 93%.

Physicochemical properties are given in Table 3.

The structure of the preparation (IV) was determined by IR spectroscopy and elemental analysis data. In the IR spectrum of the preparation (IV), the absorption bands characteristic of the RN-COO group are observed in the 1284 cm⁻¹ region; narrow bands in the region of 1719 cm⁻¹ characterize the set of stretching vibrations belonging

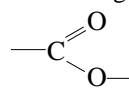



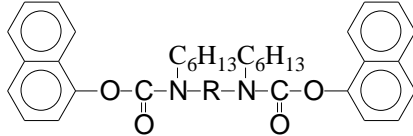
to  group in the spectra of the bis-carbamate derivative.

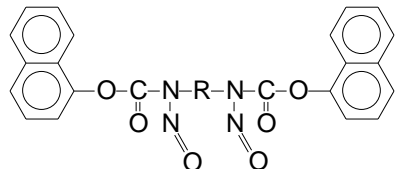
Table 3
 Physico-chemical properties of the preparation (IV)

| Structural formula | Output, % | T _{PL} , °C | R _f | Gross formula | Elemental analysis, % | | IR spectra, v, cm ⁻¹ | | | M _M |
|---|-----------|----------------------|----------------|---|-----------------------|-------|---|---|---|----------------|
| | | | | | Calculated | Found |  |  |  | |
| | | | | | N | N | | | | |
|  | 93,1 | 192-193 | 0,69 | C ₄₀ H ₅₂ N ₂ O ₄ | 4,48 | 4,27 | 1719 | 1288 | 761-719 | 624 |

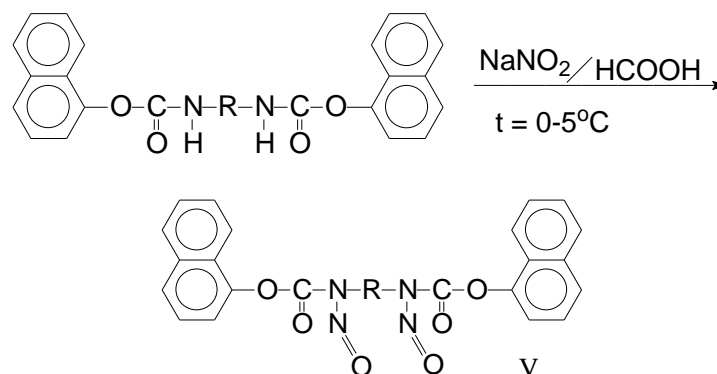
Preparation of N, N¹-dinitrosation of N, N¹-polyalkylene bis [(naphthoxy-1) carbamate] (V)

To determine the reactivity of N-H groups of substituted bis-carbamates, we conducted nitrosation reactions. As a result of the reaction of N, N¹-dinitrosation of polyalkylene bis [(naphthoxy-1) -carbamate derivatives] with sodium nitrite (in excess), the corresponding N, N¹-dinitroso-substituted bis [(naphthoxy-1) -carbamate] output 89.3%. (Table 4)

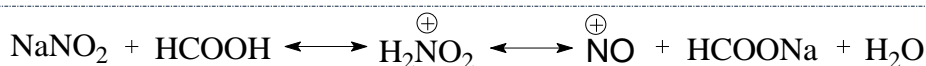
 Table 4
 Physico-chemical parameters of the preparation (V)

| Structural formula | Output, % | T _{PL} , °C | R _f | Gross formula | Elemental analysis, % | | M _M |
|---|-----------|----------------------|----------------|---|-----------------------|-------|----------------|
| | | | | | Calculated | Found | |
| | | | | | N | N | |
|  | 89,3 | 344(пас.п) | 0,64 | C ₂₈ H ₂₆ N ₄ O ₆ | 10,89 | 10,66 | 514 |

The reaction proceeds according to the following scheme:



N, N¹-dinitrosation proceeds by the mechanism of electrophilic substitution S_E. The attacking agent is nitronium ion $\text{—}\overset{\oplus}{\text{N}}\text{O}$. Since nitrous acid, which is the most common nitrosating agent, does not exist in a free form, sodium nitrite and a strong acid (conc. HCOOH) are used for this process. The resulting nitrous acid, when attached, generates an ion $\text{—}\overset{\oplus}{\text{N}}\text{O}$ the reaction proceeds according to the scheme:

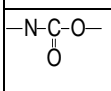





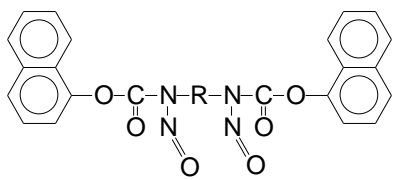


N, N¹- dinitrozosis is conducted while cooling the mixture.

The structure of the synthesized N, N¹-dinitroso-substituted is determined by elemental analysis and IR spectra. In IR spectra, absorption bands for 1550-1430 cm⁻¹ are observed, a strong absorption band, and for C = O groups is 1711 cm⁻¹, for (-CH₂) -762-721 cm⁻¹.

Thus, a method for the preparation of N, N¹-hexamethylene bis [(naphthoxy-1) -carbamate] has been developed and the chemical properties of N-H reaction centers have been studied. It has been established that the reactions of N, N¹-dichlorination, dimetallation, dialkylation and dinitrozosation occur rather with high yields.

Table 5
 IR spectra of the preparation (V)

| Structural formula | IR spectra, v, cm ⁻¹ | | | | | |
|---|---|---|--|---|---|---|
| |  |  |  |  |  |  |
|  | 1648 | 1711 | 1550-1425 | 762-721 | 2930-2856 | 1409 |

Experimental part.

The course of the reaction and the individuality of the compounds are monitored by TLC on alumina (II), the degree of activity with the appearance of spots by iodine vapor. IR spectra recorded on the spectrometer "VR-20" in KBR tablets.

Synthesis of N, N¹-hexamethylene bis [(naphthoxy-1) carbamate] (I)

24,8 g (0,2 mole) of naphthol-1 are placed in a half-liter flask, 20 ml of triethylamine, 80 ml of DMF are added, while stirring, 16,8 ml (0,1 mole) of GMI dissolved in 15 ml DMF. The reaction mixture was stirred for 4 hours at 24-30 °C. At the end of the time, the contents of the flask are transferred to a bowl, add 100 ml of water. The precipitate formed is washed and chromatographed on Al₂O₃ column. After drying, (I) is obtained: 39,81 g (95,7 % of theoretical) T_m = 181-182 °C.

Synthesis of N, N¹-disodium of substituted (I) (III)

CH₃ONa (0,036 g / mol Na and 30 ml abs. CH₃OH) is added to the flask 6,2 g (0,011 mole) (I) are added. The mixture was stirred at 23-26 °C and 2,0 hours at 40 °C. The precipitate is filtered off, washed with abs. CH₃OH, there is obtained (III). The yield was 5.2 g (83.5%). M_p = 380 °C.

Synthesis of N, N¹-dihexyl substituted (III) (IV)

5,2 g (0,01 mol) (III) is placed in a flask with 30 ml of abs. benzene, 4,24 ml (0,02 mol) of hexyl iodide are added dropwise with stirring. The mixture is stirred for 11 hours with heating in a boiling water bath, cooled and 40 ml of water are added. The precipitate is separated, recrystallized from 50 % alcohol, dried and yielded (IV) in a yield of 93,1%, T_m = 192-193 °C.

Synthesis of N, N¹-dichloro-substituted (I) (II)

6,2 g (0,01 mole) of I was placed in a flask, 60 ml of CHCl₃, 25 g of wet alumina were added and 6,0 g of calcium hypochlorite were added dropwise at a temperature of 40 °C for 1,5 hours. The reaction mixture is left to stand for 26 hours, filtered off, washed with ether and alcohol, and dried (II) in a yield of 90,6%. T_m = 151-152 °C

Synthesis of N, N¹-dinitroso-substituted (I) (V)

To 6,2 g (0,01 mol) I dissolved in 95 ml of formic acid, with constant stirring at 0-4 °C, 0,7 g of sodium nitrite is added in excess for 3,5-4 hours. After the end, poured into a glass, add water, the precipitate is filtered off, washed with benzene and dried. TLC on "Silufol" plates, yield-89,3%. T_m = 344 °C and above.

Tests for the growth-stimulating activity of the drug (I)

In the laboratory of phytotoxicology, the Institute of Chemical Technology of the Academy of Sciences of the Republic of Uzbekistan, tests were carried out for a primary evaluation of the regulating action of newly synthesized chemicals at the Tashkent Chemical-technological Institute.

Seven preparations for growth-stimulating activity were studied. Biotests were seeds of vegetable crops and cotton. A simple, fairly accurate estimate of the primary biological activity of preparations on seeds above these biotests is presented. Primary screening was performed according to Yu.V. Rakitin. This method allows you to quickly determine the degree of physiological activity of chemical compounds, which is detected by stimulation or inhibition of germination of plant seeds, as well as by changing the length of the roots and the length of the stem part.

The preparations were tested by the method of seedlocking in solutions of different concentrations followed by germination in Petri dishes. The control seeds were soaked in distilled water. In the experiments cucumbers of the variety "Uzbekistan-740", tomatoes of "Temp" variety and medium-fiber cotton of "C-6524" variety were used. The preparations were dissolved in DMSO and applied by presowing seed steeping for 18-20 hours. Three concentrations were used: 0,1; 0,01; 0,001%. The repetition of the experiments was 4-fold, the count was taken from the measurement of stem length and roots in 10-day seedlings of vegetable crops (cucumbers and tomatoes) and 7 day-old seedlings of cotton.

Table 6

Biotest of tomatoes

| Name connections | Concentration, % | Seed germination, after 5 days, % | Growth of sprouts for 10 days, % | |
|--|-----------------------|-----------------------------------|----------------------------------|-------|
| | | | root | stem |
| Control | H ₂ O, w/t | 55 | 100,0 | 100,0 |
| N,N ¹ - hexamethylene [bis (1-naphthoxyne) carbamate] | 0,1 | 40 | 88,8 | 110,0 |
| | 0,01 | 60 | 99,6 | 142,0 |
| | 0,001 | 60 | 104,1 | 118 |

The study of the preparation on growth-stimulating activity on cucumber seeds showed significant effects. Some stimulation of growth was mainly observed in the stem part of the seedlings (Table 7)

Table 7

Biotest of cucumbers

| Name connections | Concentration, % | Seed germination, after 5 days, % | Growth of sprouts for 10 days, % | |
|--|-----------------------|-----------------------------------|----------------------------------|-------|
| | | | root | stem |
| Control | H ₂ O, w/t | 85 | 100,0 | 100,0 |
| N,N ¹ - hexamethylene [bis (1-naphthoxyne) carbamate] | 0,1 | 85,7 | 107,5 | 105,2 |
| | 0,01 | 91,6 | 103,6 | 109,6 |
| | 0,001 | 97,3 | 104,2 | 116,5 |

The drug (I) (0,001%) strengthened the stem portion of the shoots by 116,5%, and above the concentration - stimulated root growth by 104,2%.

The study of the studied preparations on the growth-stimulating activity of cotton showed that the drug promoted the germination of seeds and the development of the root system of seedlings. Thus, the preparation (I) – 0,01 and 0,001% accelerated the germination of seeds (Table 8)

Table 8

Biotest of cotton

| Name connections | Concentration, % | Seed germination, after 5 days, % | Growth of sprouts for 10 days, % | |
|--|-----------------------|-----------------------------------|----------------------------------|-------|
| | | | root | stem |
| Control | H ₂ O, w/t | 100 | 100,0 | 100,0 |
| N,N ¹ - hexamethylene [bis (1-naphthoxyne) carbamate] | 0,1 | 100 | 103,0 | 108,2 |
| | 0,01 | 105 | 105,3 | 113,6 |
| | 0,001 | 108 | 115,2 | 109,5 |

The best effect on root formation was shown by the preparation (I). So in the concentration of 0,001% - 15% of the roots more than in the control. And the stimulation of the stem part of 7 day old shoots exceeded by 10% than in the control ones.

Thus, the tested preparation (I) is the most effective growth-stimulating preparation of vegetable crops and cotton in laboratory conditions, and further in-depth study in the field is recommended.

After the initial tests for the growth-stimulating activity of the preparation (I), field tests were carried out on the farm of S.Azamov in the Kasbinsk fog of the Kashkadarya region in the period from April to November 2015-2017.

The first biostimulant obtained (I), in particular, N, N¹-hexamethylene [bis (1naphthoxyne) carbamate] (I), was tested at a concentration of 0.001% (at a dilution of 750 times), in the experiments cucumbers of the grade "Uzbekistan-749", tomatoes of "Temp", medium-fibrous cotton grade "C-6524", corn and sunflower on an area of 50 hectares. An additional 101 tons of cotton was received, which is an expected economic effect of about 60 million soums only for cotton growing. Similar good results have been obtained on tomatoes, corn, cucumbers, etc. It has been established that the preparation (I) when diluted by tens of times exceeds by stimulating activity many known preparations.

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