Original Article

SYNTHESIS AND STUDY OF N,N^1 - HEXAMETHYLENE BIS-{[(4,4^1-DIMETHYLDIPHENYL)-AZO-2,2^1-DIAMINO] UREA} PROPERTIES, APPLICATIONS

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Abstract

The proposed article relates to organic chemical synthesis and the study of bis-azourea compounds, the chemical properties of new N,N1 derivatives - hexamethylene bis-[(4,41-dimethyldiphenyl)-azo-2,21-diamino) ureas]. The interaction of [(4,41-dimethyldiphenyl)-azo-2,21-diamino)-urea] with hexamethylene diisocyanate gave derivatives N,N1 - hexamethylene bis-[(4,41-dimethyldiphenyl)-azo-2,21-diamino) ureas]. The structure of N,N1 - hexamethylene bis-[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea] was established by elemental analysis, IR and PMR spectroscopy. Reactivity of NH reaction centers N,N1 - hexamethylene bis-[(4,41-dimethyldiphenyl)-azo-2,21-diamino) urea] is studied by the reactions: N,N1-dinitrosation, N,N1-dimetallation, N,N1 -dialkylation, N,N1-dichlorination. Comparative tests show that the tested derivative of the N,N1 compound - hexamethylene bis-[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea] showed a higher growth-promoting activity.

Keywords: phenyl, azogroups, urea, polyhydrocarbongroups, intensification, fixation, fabrics, natural, chemical fibers, dyes, textile, materials, dinitrosation, demetallation, dialkylation, dichlorination, polymers.

I. INTRODUCTION

Today, the modern search for the currently intensively developing chemistry and properties of bis-azourea compounds attracts the attention of many researchers, both in Uzbekistan and abroad [1-6].

II. SIGNIFICANCE OF THE SYSTEM

The paper mainly focuses on how the chemistry derivative N,N1 derivatives - hexamethylene bis-[(4,41-dimethyldiphenyl)-azo-2,21-diamino) ureas. The study of literature survey is presented in section III, Proposed methodology and discussion is explained in section IV, section V covers the experimental results of the study and Conclusion.

III. LITERATURE SURVEY

This is due, on the one hand, to the rich possibilities of azo-, phenyl, urea, and polyhydrocarbon groups in the molecules of organic macrocompounds, and, on the other hand, to the properties of the most organic compounds, valuable for practical use,

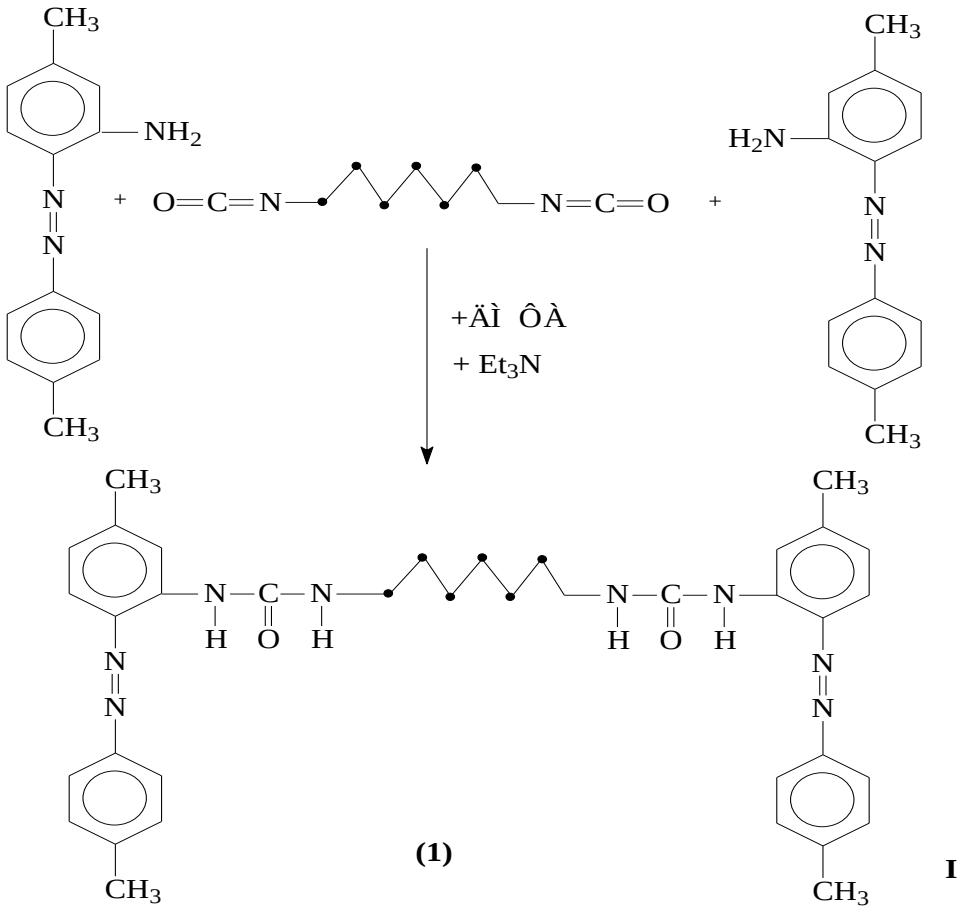
by azo-diphenyl groups and also by urea bonds. There are many examples where the introduction of azo- and phenyl-bridged bonds led to the appearance of gamma various kinds of biological, pharmacological, physiological activity, as well as the ability to inhibit the corrosion of metals, coatings and stabilizers for halogen-containing polymers, impregnations, and also as an anti-aging rubber vulcanization. Creation of solvation theory of intensification of dyeing and printing processes of fabrics from natural and chemical fibers in liquid ammonia and organic solvents. In addition, the study of the patterns of solid-phase fixation of dyes from textile materials, the creation of theoretical foundations for the use of biocatalytic systems for the processes of refining textile materials, plasma-chemical activation of fiber-forming polymers, the use of RF fields and microwave radiation in chemical-textile production [7-17]. This is due to the high reactivity to complex formation of a highly diverse functional group.

It was necessary to determine high-precision unique optimal methods for introducing azourea groups into these types of compounds and to study the dependence of the reactions used due to the mobile proton at N-H substituting functional groups.

IV. PROPOSED METHODOLOGY AND DISCUSSION

As a result, a new field of chemistry of N-H urea compounds, which was previously little studied and represented only by the simplest examples, appeared, which is a derivative of two - azo - containing bis-urea. The interaction of [(4,41-dimethyldiphenyl)-azo-2,21-diamino)-urea] with hexamethylene diisocyanate gave new N,N1 derivatives - hexamethylene bis-[(4,41-dimethyldiphenyl)-azo-2,21-diamino) ureas].

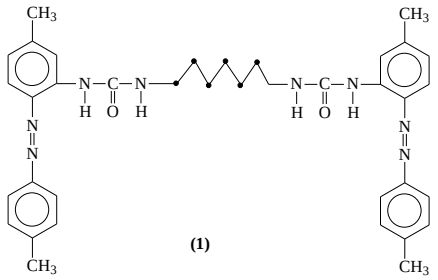
Profitable synthesis was carried out according to the scheme:



N,N[1] is hexamethylene bis-[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea].

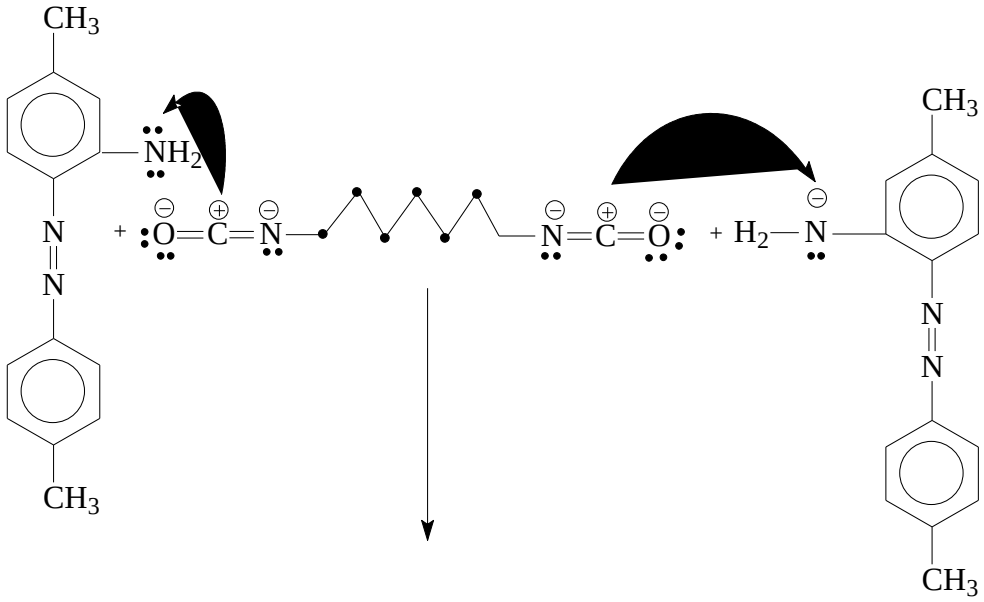
The reaction physico-chemical parameters of the drug (I) are given in table.1.

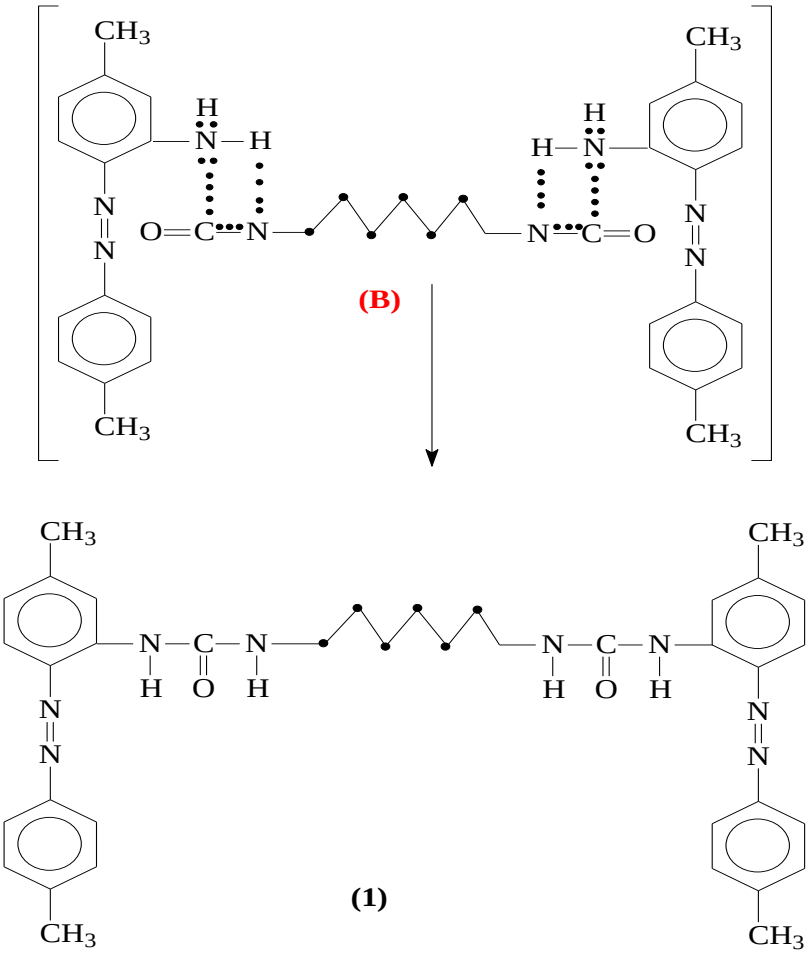
Table 1. Physico -chemical parameters of the drug (I)

Structural formula	yield, %	R_f	T mp, ^{0}C	Brutto formula	Elemental analysis, %						$M_м$
					Calculated			Found			
					C	H	N	C	H	N	
 (1)	92,6	0,76	194-195	$C_{36}H_{40}N_8O_2$	69,90	6,79	18,18	69,79	6,74	18,06	616,76

The high density, selectivity and easy mobility of the electron cloud of the group determine its high reactivity. The yield of product (1) was 92,6 %. As expected, products were obtained in good yields by the AN reaction mechanism. The physicochemical characteristics of bis-urea derivatives are apparently due to the high density and easy mobility of the electron cloud of the conjugated ( ) group, which leads to an increase in the positive charge on the carbon atom of the isocyanate group, facilitating the attack of this atom by the nucleophilic agent, and also touching on this issue , this happens due to an increase in the positive charge on the carbon atom or due to the stabilization of the transition state. However, in our cases, the –NH group of the amine, having a free pair, attacks the electrophilic center in the isocyanate molecule to form an intermediate product (B), which then rearranges into the final reaction product.

Based on our proposals and literature data, the probable mechanism of the interaction of bis [(4,41-dimethyldiphenyl)-azo-2,21-diamino)] with hexamethylene diisocyanate can be represented by the scheme:





Purification of one of the starting reagents was carried out using preparative thin-layer chromatography on Al2O3 in the system (HCOOH:CH3COCH3 :CHCl3=0.5:4.5:1.0).

To prove the structure of N,N1-hexamethylene-bis-[(4,41-dimethyldiphenyl)-azo-2,21-diamino)-], the method of IR and UV spectroscopy was applied (Table 2).

Table 2. IR and UV spectroscopy of compounds I

Compounds №	IR spectra, ɣ, cm^{-1}								UV spectra, nm		
	—N=N—	—N(H)—			—N(H)—C(=O)—N(H)—	—C(=O)—	—$(CH_2)_6$—	—CH_2—		—N=N—	
I	1551	3413	865-810	860-800	1294-1308	1690-1720	758-724	2480-2860	211	262	213

The UV spectrum of N,N1 - hexamethylene-bis [(4,41-dimethyldiphenyl)-azo-(amino)-urea has characteristic absorption bands in the region of 203-213, 260-264 nm, which corresponds in structure and name. A band appears in the spectrum in the region

of 211 nm due to the disubstituted benzene ring, and in the region of 262 nm the azo group of the phenyl-azo-toluyl group appears. This compound, specific for aromatic compounds, shifts the absorption maximum to the long wavelength region and increases its intensity. The long-wavelength part of the spectrum is due to the π-, π*-transition, which indicates the absence of a double bond in its molecule. The absorption band in the region of 211 nm is due to the excitation of electrons of the trisubstituted, and in the region of 213 nm - of the disubstituted benzene ring.

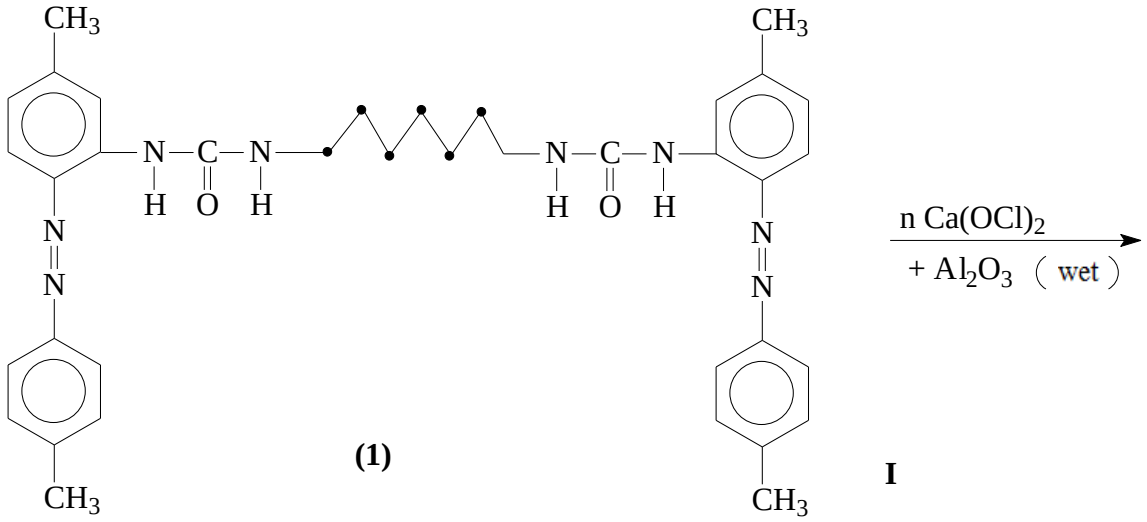
To study the reactivity at N-H reaction centers N,N1 - hexamethylene-bis [(4,41-dimethyldiphenyl)-azo-2,21-diamino) urea], we carried out rare special reactions: N,N1-dimetallation, N, N1-dialkylation, N,N1-dinitrosation and N,N1-dichlorination [18-26].

V. EXPERIMENTAL PART

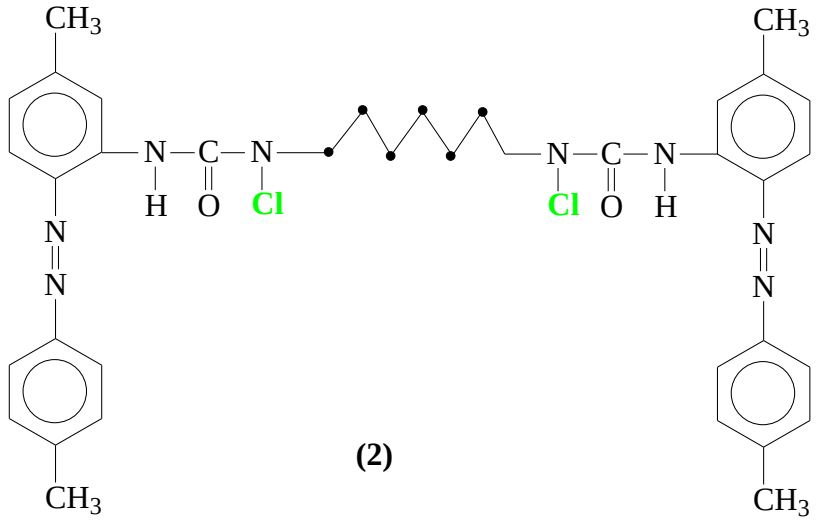
Chemical transformations of N,N1 - hexamethylene-bis [(4,41-dimethyldiphenyl)-azo-2,21-diamino) urea]. Obtaining N,N1-dichlorination of compounds (1).

N,N1 derivatives - hexamethylene-bis [(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea] (I) are the most valuable raw materials for the further synthesis of various biologically active compounds used in engineering, agriculture, and also have a high reactive center of –NH group for carrying out nucleophilic and electrophilic substitution reactions.

We have developed an efficient, affordable, cheap, stable, and environmentally friendly method for N,N1-dichlorination [15] of a bis-urea derivative with calcium hypochlorite on wet alumina:

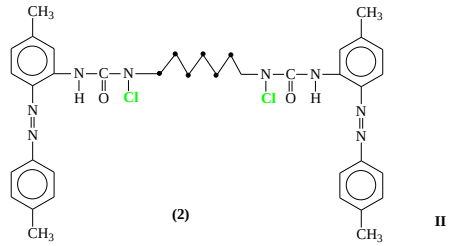


(1) **I**



(2) **II**

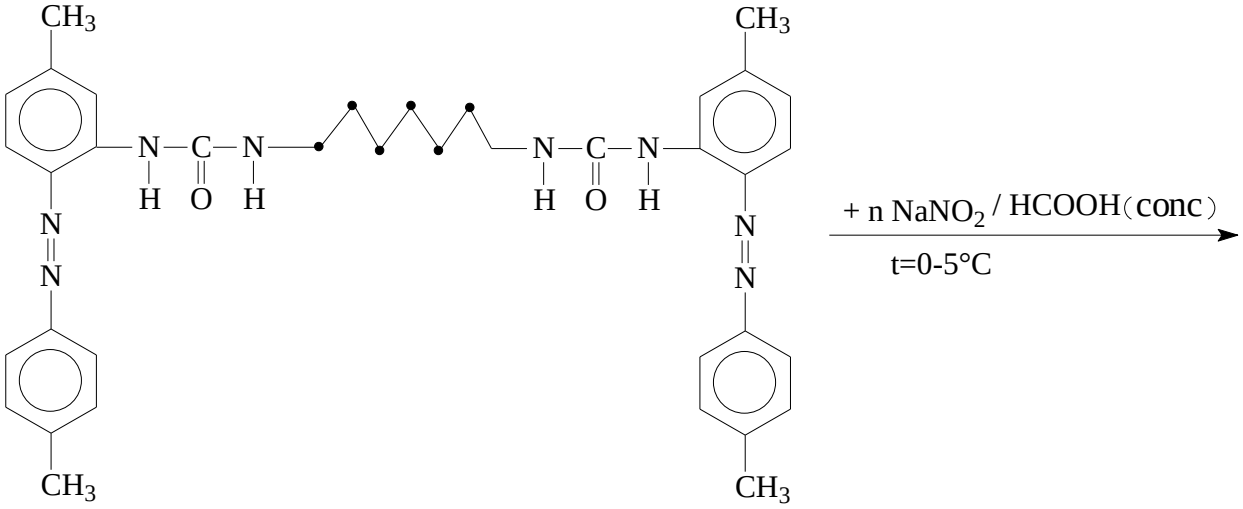
Table 3. Physico-chemical parameters of the drug (II)

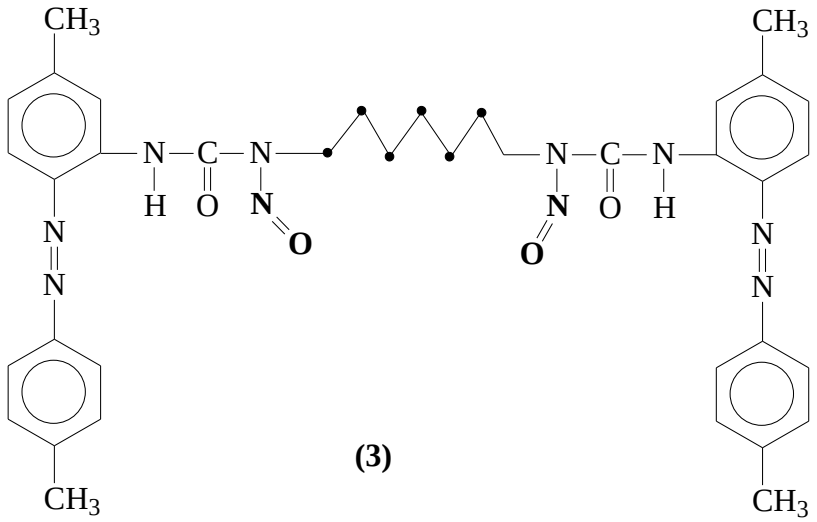
Structural formula	Yield, %	MT., ^{0}C	R_f	Brutto formula	Elemental analysis, %				$M_м$
					Calculated		Found		
					N	Cl	N	Cl	
 **(2)** **II**	90,7	148-149	0,73	$C_{36}H_{38}Cl_2N_8O_2$	16,30	10,33	16,33	10,25	685,65

The yield of compounds (II) – 90,7 %; Tm.p. = 148-1490C. Physico-chemical parameters are given in table 3.

The reaction of N,N1-dinitrosation of compounds (I).

The reaction of N,N1-dinitrosation of compounds (I) is relatively little studied in the world literature [27-32].

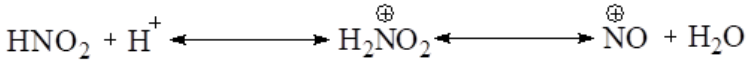




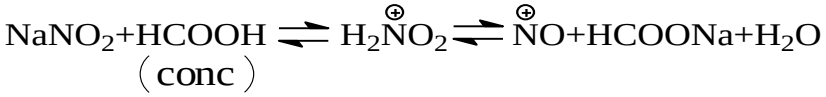
(3) **III**

According to the literature data and the data of our own research, during N-dinitrosation, nitrogen atoms react directly with the polymethylene (-CH2-)n chain. As a result of the reaction of N,N1-dinitrosation of N,N1 - hexamethylene-, bis [(4,41-dimethyldiphenyl)-azo-2,21-diamino) urea] (I) with NaNO2 (in excess) in 98% HCOOH at a temperature of 0-50C, N,N1-dinitroso substituted (1) were obtained with a yield of 90,7 %. N,N1-dinitrosation proceeds by the mechanism of electrophilic substitution (SE).

The attacking agent is the nitrosonium ion , since nitrous acid, which is the most common nitrososizing agent, does not exist in free form, sodium nitrite and strong acid (HCOOH) are used to carry out the process. The resulting nitrous acid, by attaching a proton, generates an ion .

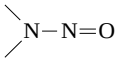
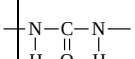


or

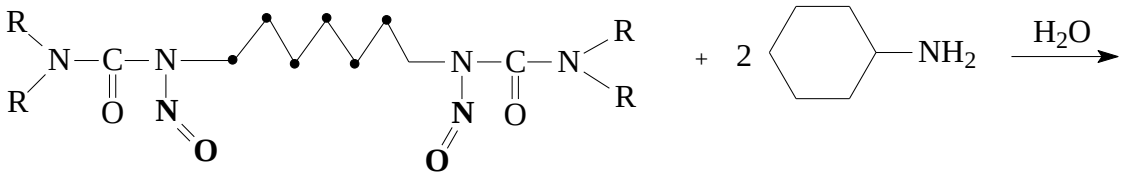


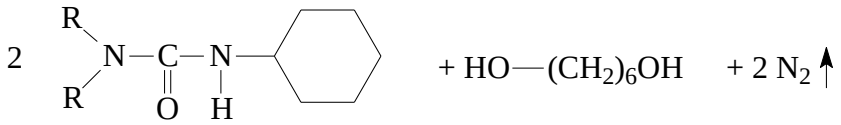
N,N1 -dinitrozonation is carried out by cooling the reaction mixture. Increasing the temperature is undesirable, since it reduces the yield of the target product, and sometimes affects the direction. Identification of N,N1 - dinitrosation of compounds is carried out by absorption bands >N-N=O groups. A characteristic band is in the region of 1500-1420 cm-1 for >N-N=O groups (Table 4).

Table 4. IR and UV spectra of compounds III

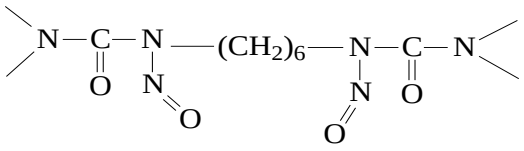
Compounds №	IR spectra, ɣ, cm^{-1}					UV spectra, nm		
	—N=N—						—N=N—	
III	1549	1500-1420	861-808	862-813	1621	214	264	220

In addition to the spectral data, the structure of N,N1 -dinitroso compounds was additionally confirmed chemically, i.e., by the reaction of N,N1 products - dinitrosation with amines [33-35]. In the interaction of N,N1-hexamethylene-bis[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea] with aqueous ammonia solutions with cyclohexylamine mono-y 1,3-disubstituted ureas were obtained:



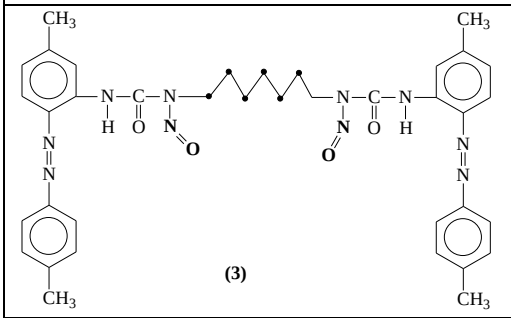


Thus, the resulting compounds prove once again that during N,N1 -dinitrosation of N,N1 - hexamethylene-bis [(4,41-dimethyldiphenyl) -azo - 2,21-diamino) urea] nitrogen atoms bound to the polymethylene chain undergo nitrosation .



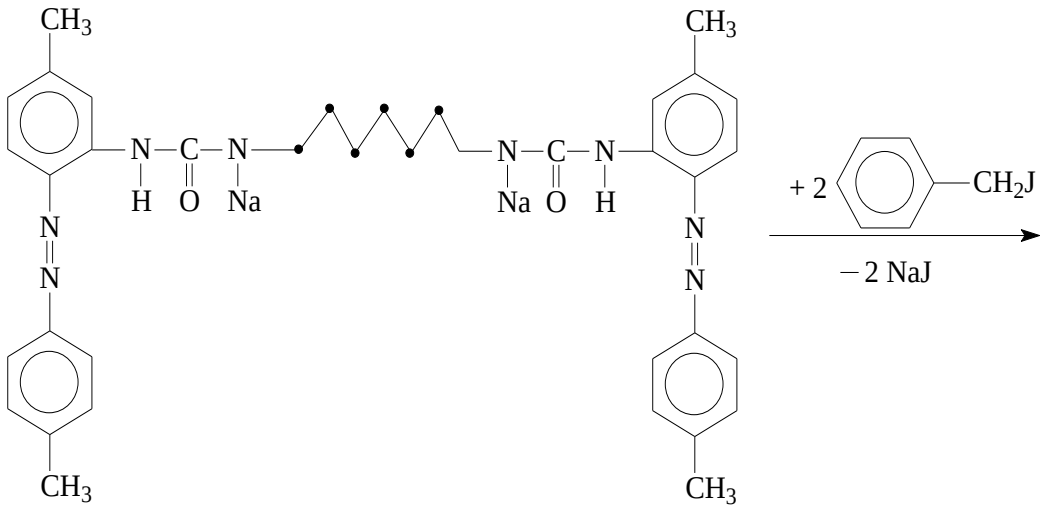
These conclusions are in good agreement with the literature data [36–38]. Physico-chemical parameters of compounds (III) are given in table.5.

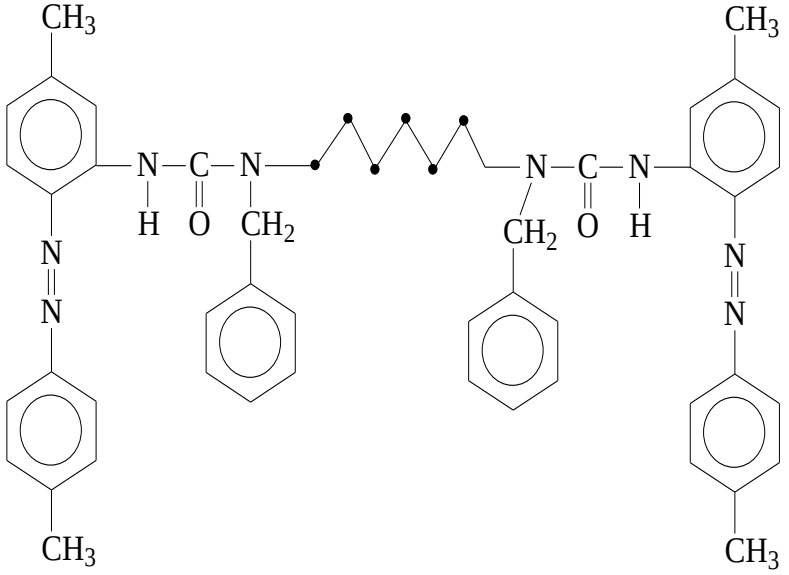
Table 5. Physicochemical parameters of compounds (III)

Structural formula	Yield, %	Tмт., ^{0}C	R_f	Brutto formula	Elemental analysis, %		M_M
					Calculated	Found	
					N	N	
 (3) III	93,5	315 (разл)	0,78	$C_{36}H_{38}N_{10}O_4$	18,76	18,69	674,75

Preparation of N,N1-dibenzyloyl substituted derivatives of compounds (I).

Dibenzylation at –NH groups in bis-ureas (I) with benzyl iodides is of undoubted interest for establishing the reactivity of containing compounds (I). Benzylation reactions were carried out by the interaction of N,N1 - disodium derivatives of N, N1 - hexamethylene with benzyl iodide in anhydrous benzene at a temperature of 35-470C and with stirring, benzyl iodide was added dropwise over 4,0-4,5 hours according to the following reaction scheme:



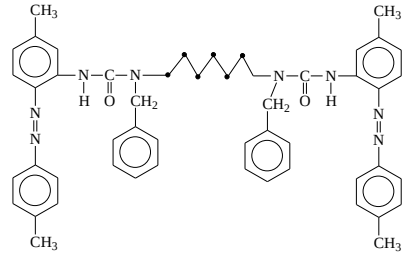


IV

The course of the benzylation reaction exclusively at the N,N1 nitrogen atom is apparently explained by the relatively easy dissociation of sodium at this atom due to the presence of neighboring carbonyl groups. The yield of the preparation (IV) was 93,4 %.

Physico-chemical characteristics of compounds (IV) are given in table.6.

Table 6. Physico-chemical characteristics of compounds (IV)

Structural formula	Yield, %	MT., ^{0}C	R_f	Brutto formula	Elemental analysis, %		$M_м$
					Calculated	Found	
					N	N	
 **IV**	93,4	204-205	0,74	$C_{50}H_{52}N_8O_2$	14,07	14,11	797,01

Experimental Part

1. Synthesis of N,N1 - hexamethylene-bis [(4,41-dimethyldiphenyl) -azo - 2,21-diamino) urea]

22,5 g (0,1 mol) [(4,41-dimethyldiphenyl) -azo - 2-amino), 60 ml of dimethylformamide, 25 ml of triethylamine were placed in a three-necked flask equipped with a reflux condenser with a calcium chloride tube, a mechanical stirrer, a thermometer and a drip funnel and 8,5 ml (0,05 mol) HMDI was added dropwise from an addition funnel with vigorous stirring. The reaction continued for 4 hours at a temperature of 23-510C. The precipitate was filtered off, washed with distilled water 2–3 times, and dried at room temperature. Appearance: whitish orange powder. Yield of product (I) 28,762 g (92,6 % of theory). Rf=0,76; Melting point = 194-1950C. The individuality of the obtained product was checked by TLC on a fixed layer (Al2O3) of II degree of purity in system 6. MM = 616,76.

Found, %:	C 69,79;	H 6,74;	N 18,06
Calculated for $C_{36}H_{40}N_8O_2$, %:	C 70,10;	H 6,54;	N 18,17

2. N, N1 nitroso-N, N1 - hexamethylene-bis [(4,41-dimethyldiphenyl) -azo - 2,21-diamino) urea]

0,13 mol of NaNO2, with stirring and cooling to 0-50C, was added in portions over 1 hour to a suspension of 6,18 g (0,01 mol) of N,N1-hexamethylene-bis[(4,41-dimethyldiphenyl)-azo-2 ,21-diamino) urea], 70 ml of 98 % formic acid, then the reaction was continued for 1 hour with stirring at the same temperature. Every 6-10 minutes, the reaction mixture was analyzed by TLC. The formed precipitate was filtered off, washed with 50 ml of ice water, and dried in air at room temperature. For methods (A-G), the filtrate was extracted with ethyl acetate (2x50 ml), washed with ice water and 5 % aqueous soda solution, dried with magnesium sulfate and evaporated to dryness. For all methods (A-G), the precipitates and residues after evaporation of the extracts were combined. The obtained N,N1-dinitroso compounds of N,N1-hexamethylene-bis[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea] were determined by Rf, washed off with acetone sorbent. The solvent was evaporated to dryness at room temperature under desiccator vacuum. The N,N1-dinitroso derivative of N,N1-hexamethylenebis[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea] was recrystallized from hexane and ethyl acetate. Yield – 6,98 g (93,5 % of theory). Tmp=3150C (dec.), Rf=0,78, Mm=674,75.

Found, %:	C 67,49;	H 5,01;	N 18,69
Calculated for $C_{36}H_{38}N_{10}O_4$, %:	C 64,08;	H 5,67;	N 20,76

3. N,N1-dichloro-N,N1-hexamethylene-bis[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea]

6,18 g (0,01 mol) of N,N1-hexamethylene-bis[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea], 60 ml of carbon tetrachloride, 26,0 g of wet alumina were placed in a three-necked a flask equipped with a reflux condenser with a calcium chloride tube, an auto-mixer and a thermometer, and 4,8 g of calcium hypochlorite were added dropwise at 37°C for 4 hours. Then the reaction mass was left for 30 hours. The precipitate that formed was filtered off and washed with ether. Received 6,23 g (90,7 % of theoretical); Rf=0,73, Tmp.=148-149 0C. Mm=685,65.

Found, %:	C 62,33;	H 5,67;	N 16,33;	Cl 10,52
Calculated for $C_{36}H_{38}Cl_2N_8O_2$, %:	C 63,06;	H 5,58;	N 16,34;	Cl 10,34

4. N,N1-dibenzylo-N,N1-hexamethylene bis[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea]

3,1 g (0,01 mol) of N,N1- disodium -N,N1- hexamethylene bis[(4,41-dimethyldiphenyl) – azo -2,21 -diamino) urea] in 33 ml of benzene were placed in a three-necked flask, equipped with a reflux condenser with a calcium chloride tube, an auto-mixer and a thermometer. 2,4 g (0,02 mol) of benzyl iodide was added dropwise with slow stirring. The mixture was then stirred for 13 hours while heated in a boiling water bath. After cooling, 25 ml of water was added, the precipitate was separated and recrystallized with 50 % alcohol. Received 7,43 g (93.4% of theory); Rf=0.74; Tmp=204-205 0C; Mm=797,01 g.

Found, %:	C 75,22;	H 6,41;	N 14,11;
Calculated for $C_{50}H_{52}N_8O_2$, %:	C 75,35;	H 6,57;	N 14,06;

5. N,N1-diisopropyl -N,N1-hexamethylene bis[(4,41-dimethyldiphenyl)-

azo-2,21-diamino)urea]

Similarly, by the method described above, the following were obtained: N,N1-diisopropyl -N,N1-hexamethylene bis [(4,41-dimethyldiphenyl) -azo - 2,21-diamino) urea] - with a yield of -94,7 %; Tmp = 187-180 0C.

CONCLUSION

Growth-stimulating activity of the drug (I)

To identify the growth-stimulating activity of N,N1-hexamethylene bis[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea] compounds, tests were carried out in the laboratory of the Institute of Chemistry of Plant Substances of the Academy of Sciences of the Republic of Uzbekistan in laboratory conditions, vegetable and cotton seeds were biotests.

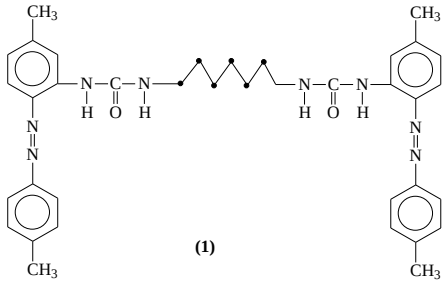
In the experiments, cucumbers of the "Uzbekistan-740" variety, tomatoes of the "Temp" variety and medium-staple cotton of the "C-6524" variety were used. The preparations were dissolved in DMF and used by the method of presowing seed locking for 18-20 hours. The concentrations used were -0,1; 0,01; 0,001; 0,0001 and 0,00001 %. The repetition of experiments is 4-fold. The counts were carried out by measuring the length of the stem and root of 10-day-old cotton seedlings. It was noted that all preparations tend to stimulate the growth of the root systems of young seedlings, both vegetables and cotton.

Primary screening was carried out according to the method of Yu.V. Rakitin. This method allows you to quickly determine the degree of physiological activity of chemical compounds, which is revealed by the stimulation or inhibition of the germination of plant seeds, as well as by changes in the length of the roots and the length of the stem part. The preparations were tested by the method of seed locking in solutions of different concentrations, followed by germination in Petri dishes. Control seeds were soaked in distilled water.

Each series of experiments is accompanied by control. In control variants, only a pure solvent is added to the nutrient medium.

The result of the experiments is recorded after 3,5,7 and 10 days after inoculation (table 7)

Table 7. Influence of preparations (1) on the germination of seeds and the growth of seedlings of cotton varieties "C-6524"

Experiences / A drug **(I)**	Concentration, %	Germination, %	Cotton	
			Root growth, %	Stem Growth, %
Control - water	without	80,0	100,0	100,0
 **(1)**	0,1	89,2	114,5	110,4
	0,01	87,7	116,3	129,6
	0,001	88.4	137,5	144,3
	0,0001	85.6	133,7	127,6
	0,00001	84,2	126,8	111,3
«Roslin» (famous)	0,75-1,0	82,3	102,4	103,3

Comparative trials also show that the test product (I) i. derivative of N,N1-hexamethylene bis[(4,41-dimethyldiphenyl)-azo-2,21-diamino)urea] from 7,5-75000 times lower concentration of our drug, showed higher growth-stimulating activity than currently used in many branches of agriculture of the Republic, the drug "Roslin". The preparation (I) showed biological activity on the cotton crop, at a concentration of 0,00001 % (at a dilution of 75,000 times) stimulated root growth by 126,8 %, and stem growth by 111,3 % higher than the control and the well-known drug "Roslin" concentration 0, 75-1,0 %.

The preparation (I) on tomatoes, similarly to previous cultures, showed a very high biological activity of 126,4 % above the control at a concentration of 0,00001 % (in a dilution of 75,000 dilutions) (Table 8).

The preparation (I) also showed biological activity on cucumber culture.

Thus, low toxicity (LD50 - 4080-4100 mg/kg) drug (I) showed high stimulating properties on the seeds of tomato, cucumber and cotton at 0,00001 % concentration.

Table 8. The effect of the drug (I) on the germination of seeds and the growth of seedlings of tomato variety "Temp".

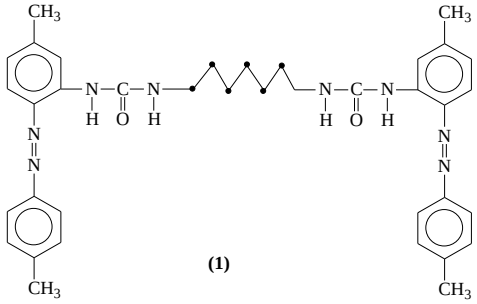
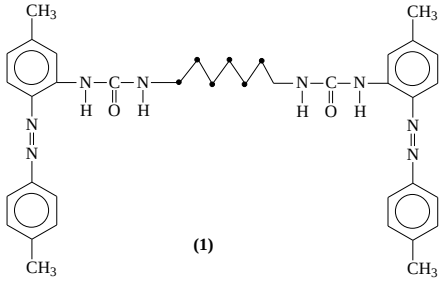
Experiences / A drug **(I)**	Concentration, %	Germination, %	Tomatoes	
			Root growth, %	Stem Growth, %
Control - water	б/о	50,0	100,0	100,0
 **(1)**	0,1	53.4	106,3	116,0
	0,01	59,7	117,7	124,6
	0,001	67,8	149,6	130,4
	0,0001	62,4	133,4	123,2
	0,00001	60,3	126,4	114,7
«Roslin» (famous)	0,75-1,0	52,1	101,9	100,7

Table 9. The effect of the drug (1) on the germination of seeds and the growth of seedlings of cucumber varieties "Uzbekistan-740".

Experiences / A drug **(I)**	Concentration, %	Germination, %	Cucumbers	
			Root growth, %	Stem Growth, %
Control - water	б/о	100,0	100,0	100,0
 **(1)**	0,1	100,0	110,3	114,7
	0,01	100,0	114,6	117,5
	0,001	100,0	127,3	115,7
	0,0001	100,0	134,6	119,6
	0,00001	100,0	142,4	123,4
«Roslin» (famous)	0,75–1,0	100,0	103,4	101,8

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