

SYNTHESIS AND SPECTRAL CHARACTERIZATION OF NOVEL BIS-UREA DERIVATIVES BASED ON HEXAMETHYLENE DIISOCYANATE AND TOLUIDINES

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Abstract. *This study describes the synthesis, structure, and physicochemical properties of N^2,N^3 -hexamethylene-bis-[(o-, m-, p-toluidinyl)urea], a novel bis-urea compound. The synthesis was carried out through the reaction between o-, m-, and p-toluidine and hexamethylene diisocyanate (HDI). The structures of the obtained compounds were confirmed by elemental analysis and FT-IR spectroscopy. The synthesized derivatives were obtained in high yields and exhibited characteristic spectral features corresponding to urea functional groups.*

Keywords: *bis-urea, toluidine, hexamethylene diisocyanate, synthesis, isocyanate, amine addition reaction.*

Introduction

Urea and its derivatives play an important role in organic chemistry and are widely used in various fields, including agriculture, medicine, polymer science, and materials engineering [1–5]. In particular, bis-urea

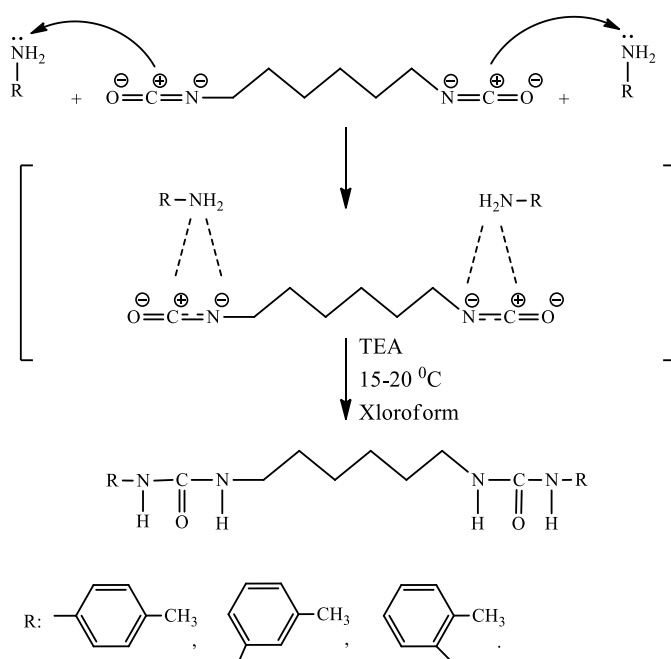
compounds have attracted considerable attention due to their high reactivity and diverse functional properties.

Hexamethylene diisocyanate (HDI) belongs to the class of aliphatic diisocyanates and is extensively used in the synthesis of polyurethanes, polyureas, and other polymeric materials [6–8]. The aliphatic structure of HDI provides excellent ultraviolet stability and color retention properties, making it suitable for coatings, automotive applications, and various industrial uses [9].

The o-, m-, and p-isomers of toluidine (methylaniline) belong to the family of aromatic amines and readily react with isocyanates to form urea derivatives. Due to their electron-donating properties, toluidine isomers effectively participate in reactions with isocyanate groups, leading to the formation of stable urea products [10–12].

Experimental Section. Synthesis of N²,N³-Hexamethylene-bis-[(o-, m-, p-toluidinyl)urea]

The target compounds were synthesized according to the following reaction scheme:



The synthesis of N²,N³-hexamethylene-bis-[(o-, m-, p-toluidinyl)urea] derivatives was carried out in a three-necked round-bottom flask equipped with a mechanical stirrer, thermometer, and dropping funnel for continuous reagent addition.

Initially, o-, m-, or p-toluidine was introduced into the reactor. For example, 0.2 mol (2.15 g) of p-toluidine was dissolved in 50 mL of chloroform. The resulting mixture was stirred at 30°C until a homogeneous solution was obtained.

Subsequently, 5 mL of triethylamine was added as a catalyst, followed by the slow dropwise addition of 0.1 mol (2.28 g) of hexamethylene diisocyanate over a period of 30–40 minutes.

The reaction temperature was then reduced to 15–20°C, and the mixture was continuously stirred for 4 hours. As the concentration of diisocyanate increased, the formation of white precipitates corresponding to N²,N³-hexamethylene-bis-[(o-, m-, p-toluidinyl)urea] derivatives was observed.

After completion of the reaction, the system was allowed to stand for 24 hours. The liquid phase consisting of chloroform and excess starting materials was removed using a separatory funnel. The resulting urea derivatives were filtered and dried under vacuum at a residual pressure of 0.5–1.5 kPa until constant weight was achieved.

The crude products were purified by recrystallization from ethanol. Colorless crystalline compounds were obtained.

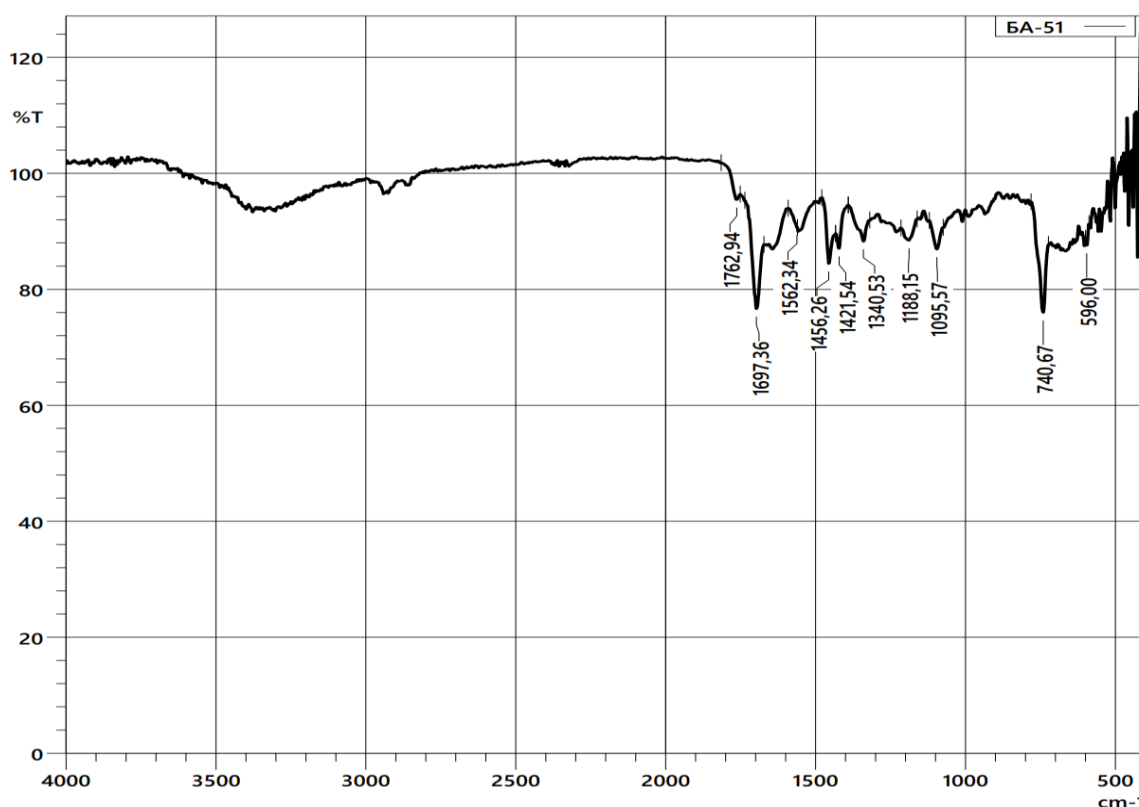
Yields of Synthesized Products

Compound	Yield (g)	Yield (%)
N ² ,N ³ - Hexamethylene-bis- [(o-toluidinyl)urea]	2.98	77.8

N ² ,N ³ - Hexamethylene-bis- [(m-toluidinyl)urea]	3.05	79.6
N ² ,N ³ - Hexamethylene-bis- [(p-toluidinyl)urea]	3.20	83.7

To confirm the structures of the synthesized bis-urea derivatives, FT-IR spectra were recorded and analyzed.

Results and Discussion. The FT-IR spectrum of N²,N³-hexamethylene-bis-[(p-toluidinyl)urea] exhibited characteristic absorption bands corresponding to the expected functional groups.



1-figure. IR spectrum of N²,N³hexamethylene-bis-[(p-toluidinyl)urea]

Strong absorption bands at 1762.94 cm^{-1} and 1697.36 cm^{-1} were assigned to the stretching vibrations of the carbonyl group $\nu(\text{C=O})$, indicating the presence of urea fragments. The absorption band at 1562.34 cm^{-1} corresponds to aromatic $\text{C}=\text{C}$ vibrations and N-H deformation modes. Bands observed at 1456.26 cm^{-1} and 1421.45 cm^{-1} are attributed to methylene ($-\text{CH}_2-$) groups and aromatic skeletal vibrations. The absorption peak at 1340.53 cm^{-1} is characteristic of C-N stretching vibrations. Additional bands at 1188.15 cm^{-1} and 1095.57 cm^{-1} are associated with C-O-C and C-N stretching vibrations. The signal at 740.67 cm^{-1} corresponds to out-of-plane deformation vibrations of aromatic C-H bonds. Overall, the FT-IR spectral data confirm the presence of carbonyl, urea, and aromatic ring fragments within the synthesized molecule and support the proposed molecular structure.

Conclusion. Novel N^2, N^3 -hexamethylene-bis-[(o-, m-, p-toluidinyl)urea] derivatives were successfully synthesized through the reaction of hexamethylene diisocyanate with o-, m-, and p-toluidines. The reactions proceeded with relatively high yields ranging from 77.8% to 83.7%.

The structures of the synthesized compounds were confirmed by FT-IR spectroscopy. The obtained bis-urea derivatives represent promising candidates for applications in coordination chemistry, corrosion inhibition, and the development of biologically active materials.

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