



Original Research article

Synthesis and Characterization of New Diamine Based on Fluorine



Ali Sadeghinia, Hossein Mighani*

Faculty of Science, Department of Chemistry, Golestan University, Gorgan, P.O.Box 155, Iran

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KEYWORDS

Diamine

Thermo-resistant polymer

Polyamide

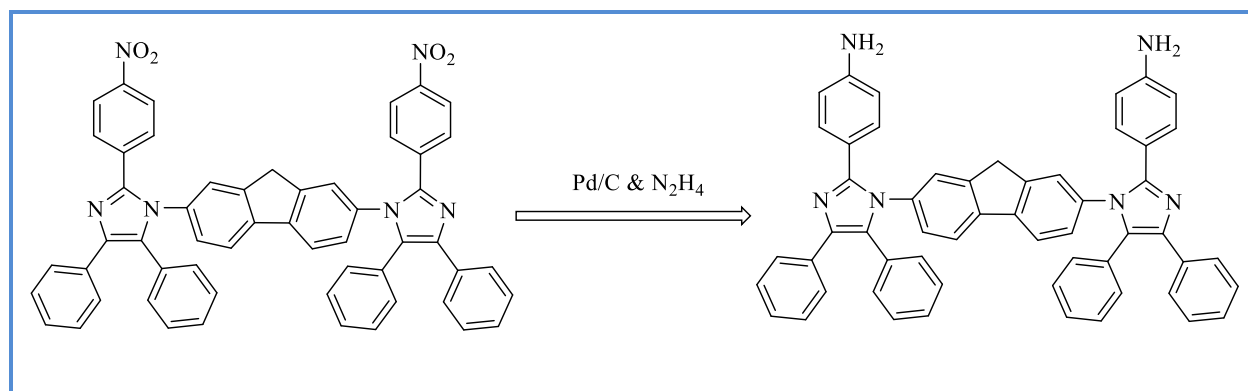
Polyimide polyurea and polyurethane

ABSTRACT

Aromatic and aliphatic diamines are key components in polyamides, polyimides, polyurea and polyurethanes. To prepare high performance and well-featured materials, attempts are directed to synthesize novel diamine in which thermo-resistant, soluble and easy-process polymers are obtained. To improve the solubility and decrease the glass transition temperature, flexible bonds are necessary for the polymer-repeating unit. These bonds decrease the internal rotational energies. In this sense, by using the heterocyclic rings as well as introducing polar functional groups such as amide in the main synthetic polymer chain, convenient polarity and solubility of the polymers are reached. Till now, extensive investigations have been conducted to prepare the aromatic monomers with high solubility and processing capabilities. In the current study, our main aim is to prepare diamines with applications in thermo-resistant polymers such as polyamide, polyimide, polyurea, and polyurethanes.

*Corresponding author: E-mail: h.mighani@gu.ac.ir, Faculty of Science, Department of Chemistry, Golestan University, Gorgan, P.O.Box 155, IranTel: +98 17 32245964

Graphical Abstract



Introduction

Amines, as the main components of amino acids, peptides and nitrogen compounds, are the most abundant organic molecules. Primary and secondary amines are less acidic and form weaker hydrogen bonds with alcohols and ethers than alkaloids. On the contrary, they have stronger bases and nucleophiles as compared to alcohols and ethers. Diamines are amines with two functional amine groups. Hexamethylenediamine is an essential amine for the nylon manufacture industry. The mentioned amine reacts with adipic acid to produce nylon 6, 6. This nylon is used to manufacture socks, stretch clothes and textile fibers. Many investigations have been performed on diamines, some of which are cited here in this paper. The effect of EDTA and municipal solid waste compost on different amounts of lead and cadmium in soil and plant decontamination of these elements by sunflower was investigated by [1]. A cationic catalyst of the iron complex has catalyzed amination of aryl-aziridine to produce a high yield diamine. This method is compatible with both of the existing functional groups in amine and aziridine [1]. Amination of meso-en-phenyl aziridine is improved using 1 wt% of the mentioned catalyst to produce a high-yield diamine [2]. One can prepare racemic and non-racemic tetrahydroquinoxaline using this procedure: activating aziridine through an S_N2 ring opening reaction utilizing bromo-aniline in the presence of palladium as a catalyst, forming an intermolecular C-N bond, and selecting a stereoselective path [3].

Dinuclear iodine (III) can promote intermolecular amination of alkanes. This reagent can progress the reaction by the formation of chiral imido-iodine intermediate [4]. Using copper chloride as a catalyst and ditertiary butyl thiaziridionine as a nitrogen source provides a mild condition to an efficient amidation of olefins [5]. Wide ranges of olefins may participate in diamination reaction through allylic and homo-allylic carbon activation. Such a stereoselective reaction is performed

using ditertiary butyl aziridinone as a nitrogen source and trephenyl palladium as a catalyst [8]. Asymmetric diamination of a dien alkyl *N,N*-di-tertiary-butyl thiadiaziridine1,1-dioxide in the presence of palladium and chiral phosphoramidite ligand yields cyclic sulphamide [9]. Diamination of non-reactive alkenes with en-fluorobenzene sulfonamide (NFBS) as nitrogen donor was studied by [10]. Diamination through an intermolecular reaction catalyzed by palladium led to the formation of urea. Urea is necessary for the oxidative conversion of alkene in the presence of iodosobenzene as oxidative reagent [11]. In current study, we deal with synthesis and characterization of novel monomer which are used in various polymers. Diol, diacid, diisocyanate and diamines are typical monomers which are applicable in preparation of different polymers including polyamide, polyurethane and polyimides. Diamines dealing with here are one of the most important monomers which have been used during recent years. There are two kinds of diamines: aliphatic and aromatic diamines. Polymers prepared from aromatic monomers are commonly more thermo-resistant and less soluble. Therefore, semi-aromatic diamines seem to be more soluble than aromatics. Therefore, synthesis of semi-aromatic diamines is the aim of many investigations. Because they have suitable thermal resistance and solubility.

Experimental

Chemicals and method

Used chemical with their assays are listed in Table 1.

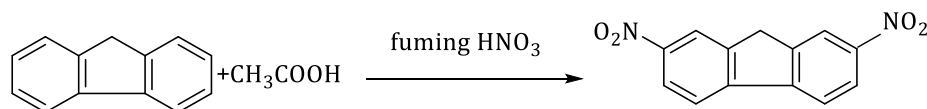
Table 1. Composition, trademarks, company and assay

Composition	Trademarks	Company	Assasy%
Flourene	-	Sigma aldrich	99
Acetic acid	AcOH	Merck	99
Sodium chloride	NaCl	Sigma Aldrich	99
Nitric acid Fuming	-	Merck	99
Paladium	Pd	Merck	10
Benzyl	-	Merck	98
4-Nitrobenzaldehyde	-	Merck	99
Ammonium acetate	-	Merck	99
Hydrazine hydrate	-	Merck	98
n-methylpyrrolidone	NMP	Merck	99
pyridine	-	Merck	99
Tetrahydrofuran	THF	Merck	99
Isophthaloy dichloride	IPC	Merck	99

Fluorene based diamine synthesis

Synthesis of 2,7-dinitrofluorene

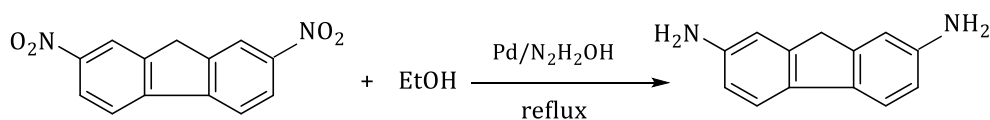
Firstly, a mixture of 10 g (0.06 mol) fluorene and 50 mL glacial acetic acid at 0-5 °C was entered into a three neck balloon equipped with mechanical stirrer while stirring for 0.5 h. While the solution was stirring, 50 mL fuming nitric acid was added during 45 min. Reaction temperature after nitric acid addition ascended to 65 °C and after that we allowed the mixture to cool down and stand along the night. An orange precipitate is formed through this procedure. After that, the mixture was transferred to the 500 mL water/ice and stirred for 1 h. The mixture was filtered and washed several times with deionized water. The product was dissolved in 150 mL chloroform and after washing several times with water and salt then the orange phase was separated and dried with magnesium sulfate. After solvent removal, orange viscose phase was separated and dissolved in 100 mL hexane. After placing the container into ice-water, the yellow precipitate which is related to 2,7-dinitro fluorene was appeared. Yield of reaction was 79% and melting point was about 295-300 °C.



Scheme 1. Synthesis of 2,7-dinitrofluorene

Synthesis of 2,7-diaminofluorene

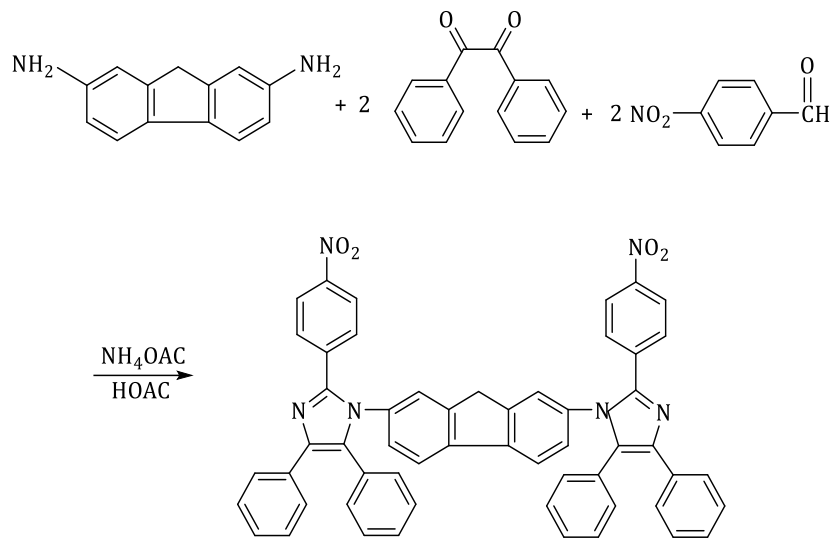
Second step is the reduction of dinitro product. A mixture of 7 g (0.028 mol) 2,7-dinitrofluorene, 0.5 g Pd/C (5%) and 150 mL absolute ethanol was added to a three neck balloon equipped with mechanical stirrer while refluxing. Then 20 mL hydrazine hydrate 85% mixed with 25 mL ethanol was introduced into the balloon dropwise during 1.5 h. The mixture was refluxed for 2 h and during refluxing time, another 0.1 g of fresh catalyst added at different distances. When reaction was completed, the mixture was filtered and resultant solution was transferred to cold water in which 2,7-diaminofluorene precipitated. After washing with water, final product was dried at 60 °C for 5 h. Yield of reaction was about 94% with melting point of 160-163 °C.



Scheme 2. Synthesis of 2,7-diaminofluorene

Fluorene based dinitro synthesis

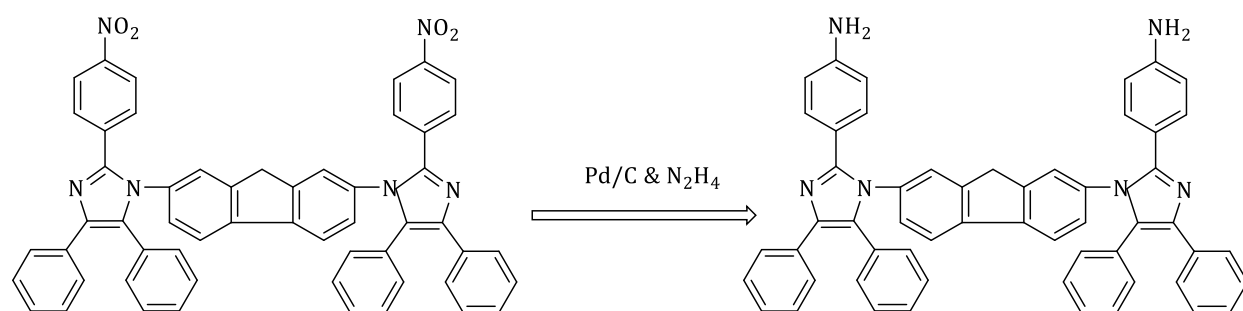
To prepare fluorene based dinitro, 1 mmol 2,7-diaminofluorene, 2 mmol benzyl, 2 mmol ammonium acetate were entered into a three neck ballon equipped with stirrer and condenser and 10 mL acetic acid was added as well. The mixture was refluxed for 12 h at 120 °C. After cooling, filtering and washing with methanol, the final product was dried at 90 °C for 5 h. Obtained yellow precipitate had a 335-340 °C melting point.



Scheme 3. synthesis of fluorene based dinitro

Fluorene based diamine synthesis

A mixture of 7 g (0.028 mol) 2,7-dinitrofluorene, 0.5 g palladium/C (5%) and 150 mL ethanol was transferred to a 250 mL balloon equipped with stirrer and condenser while refluxing. 20 mL hydrazine hydrate (85%) dissolved in 25 mL ethanol was drop wise added to the reaction container during 1.5 h. The mixture was refluxed for 2 h and during refluxing time another 0.1 g off rest catalysis added at different distances. After filtering, obtained precipitate was dried at 60 °C for 5 h. Then the precipitate was dissolved in 100 mL THF and refluxed at 70 °C. After filtering, the resultant solution was transferred to the cold water and opaque white crystallized product appeared. Then precipitate was dried at 60 °C for 5 h. Yield of reaction was 78% and the melting point was about 245-248 °C. In IR spectrum, the existing peaks in region of 3452 cm^{-1} and 3369 cm^{-1} prolongs to NH_2 group and the peaks in region of 3020 cm^{-1} and 1473 cm^{-1} are related to aromatic C-H and C=N groups, respectively.



Scheme 4. synthesis of fluorene based diamine

Results and discussion

Characterization of fluorene based diamine

To characterize the prepared sample, IR and NMR spectroscopy were used. Peaks in the region of 3347 cm^{-1} and 3306 cm^{-1} are related to stretching vibration of NH_2 . Aromatic C-H vibration peaks appear in 2919 and 3033 cm^{-1} . Corresponding stretching vibration peaks of C=C are in 1472 and 1376 cm^{-1} and peaks in 1279 and 1634 cm^{-1} are assigned to C-N and C=N vibrations.

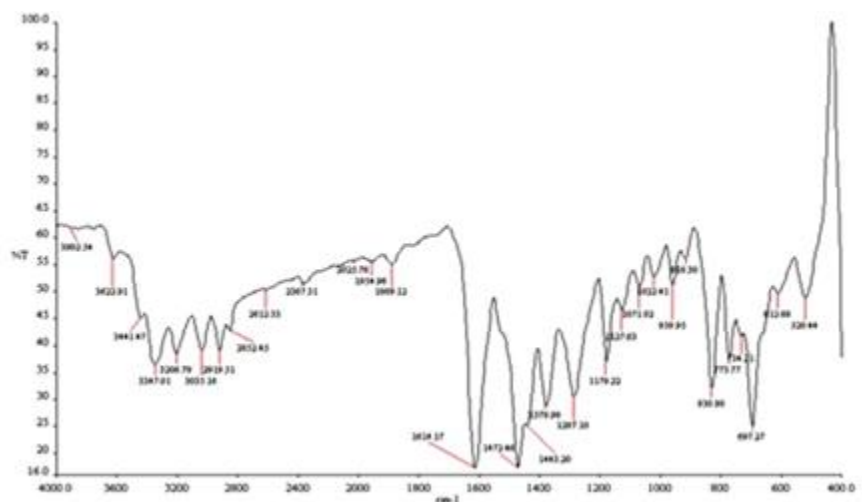


Figure 1. Spectrum FT-IR of fluorene based diamine

In NMR spectrum, a peak in 5.2 ppm is related to NH_2 . With envisaging the fact that, two NH_2 groups are present in structure and if the peak areas relating to these two NH_2 groups are considered, one can conclude that the peaks higher than 6 ppm are related to aromatic hydrogens while the integration of these peak areas is equal to 34 verifying the number of aromatic hydrogen's. A peak in 2 ppm is related to methylene hydrogen which has been splitted due to diastereotopic effect. Integration of peak areas was 2 proving the number of methylene hydrogen's.

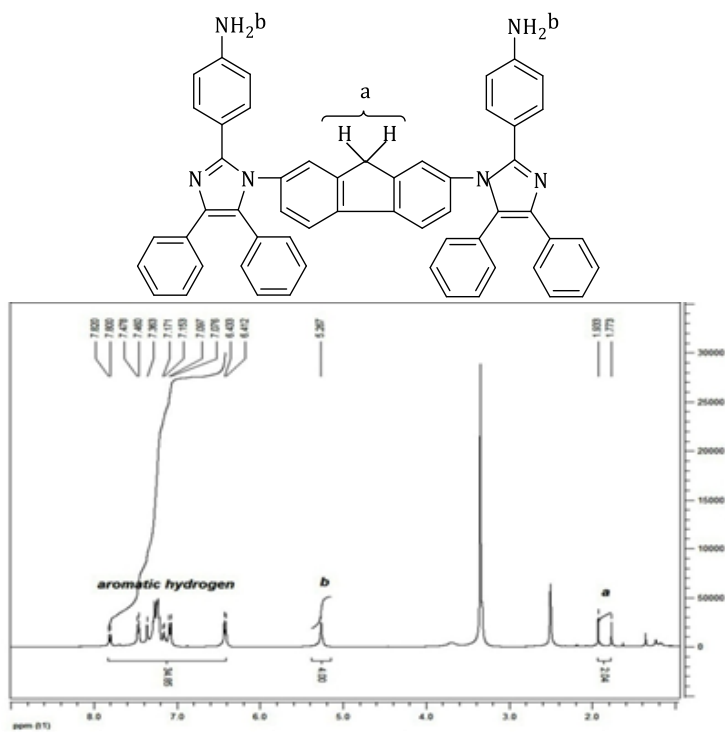


Figure 2. Spectrum ¹H NMR of fluorene based diamine

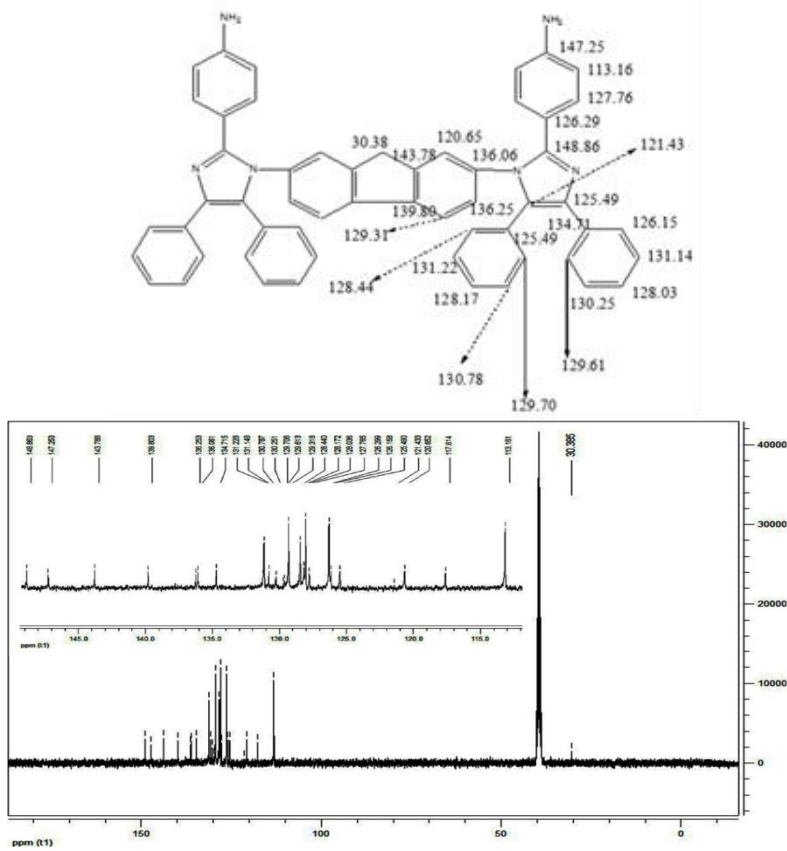


Figure 3. Spectrum ¹³C NMR of fluorene based diamine

Conclusions

Dinitrofluorene was synthesized using fluorene and then diamino fluorene was prepared. Using this material together with benzyl and *p*-nitrobenzaldehyde, a novel fluorene based amine was prepared and its structure was characterized by FTIR, ¹HNMR and ¹³CNMR.

Acknowledgment

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Conflict of Interest

We have no conflicts of interest to disclose.

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