

## A Novel Route of Synthesize the Monomer 3,6- Di-iso cyanato N-neopentyl Carbazole and its Photo-conducting Polymers with Resorcinol and Bisphenol-A.

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**Abstract:** The novel monomer 3,6- Di-iso cyanato N-neopentyl carbazole has been synthesized and the monomer has been characterized by IR, UV and NMR spectra. Two polyurethanes by the reaction of 3, 6- Di-iso cyanato N-neopentyl carbazole with resorcinol and bisphenol-A have been synthesized and the corresponding polymers have been characterized by IR, UV and NMR spectra.

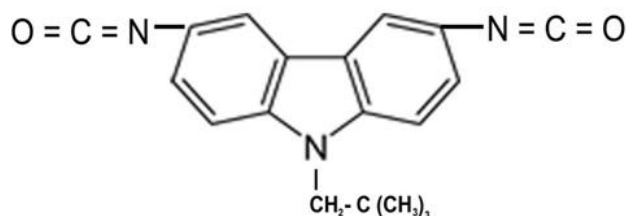
**Keywords:** 3, 6- Di-iso cyanato N-neopentyl carbazole Polyurethanes, polymerization process.

### I. Introduction:

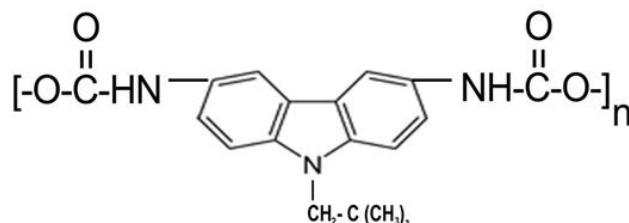
Polymers with carbazole group are of considerable scientific and industrial interest because of their attractive features, such as their hole transporting, high charge carriers and electroluminescent properties. The hole transporting ability of carbazole containing polymers make them especially useful for application in organic electronics. Numerous studies have been devoted to carbazole-containing polymers as a result of the success of poly (N-vinyl carbazole), poly (NVC), in electro photographic applications. Recent developments in this field are mostly connected to applications in polymeric light-emitting diodes, organic photo refractive materials, and photovoltaic devices.

For example, conjugated poly (3, 6- carbazole) and poly (2, 7- carbazole) derivatives having carbazole moieties in the main chain have been employed for application in solar cells and white –light-emitting diodes. In the past few decades, considerable attention has been given to the self –assembly of block copolymers, because of their feasibility of using them to generate nano structured materials and their numerous potential applications in separation technology, control drug delivery and release, and smart catalyst separation technology.

A large number of photo conducting polymers have been synthesized using different kinds of polycyclic homo or hetero atomic aromatic compounds. In some cases aromatic groups are pendant from different kinds of polymeric back-bone, but still poly vinyl carbazole is the most important one with respect to efficiency and cost of preparation. It is known that photon absorption by polymer can generate charge carriers under external electric field and suitable carrier injectors. Polymeric organic photoconductors mostly follow hopping mechanism of conduction. The hopping mechanism is well dependent on structural sequence and regularity of the polymer. In general, polymeric compound are comprised of amorphous phase fully or partially. The relationship between mechanism of photo-ionization, photo- conduction and trapping of charge carriers with respect to structure is not well established. All these studies have been made very arbitrarily. In this article, the monomer 3,6- Di-iso cyanato N-neopentyl carbazole has been synthesized.



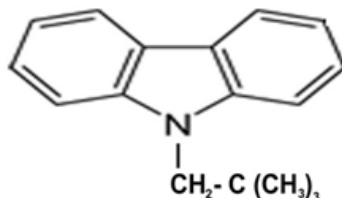
Then preparation of polymers of 3,6-Di-isocyanato N-neopentyl carbazole with resorcinol and bisphenol-A of the following structure.



## II. Experimental:

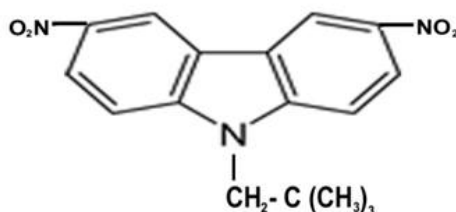
### 2.1 preparation of N-neopentyl carbazole:

In an oven dried, one liter round-bottomed flask equipped with a magnetic stir bar and a rubber septum are placed carbazole and sodium hydroxide pellets in dry acetone, under an argon atmosphere. Stoichiometric amount of neopentyl bromide is added slowly over 15 minutes to the stirred reaction mixture at room temperature. After the addition, the reaction mixture is stirred for 8 h at which time all solids are removed by filtration. The product is purified by repeated crystallization. The product is characterized by checking the melting point and verifying IR, UV and NMR spectra.



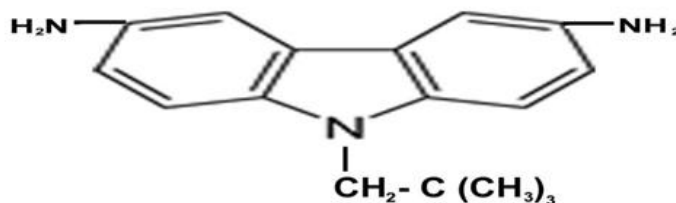
### 2.2 Preparation of 3, 6-Di-nitro N-neopentyl carbazole:

To a solution of 20g copper (II) nitrate hemi pentahydrate in a mixture of acetic acid (40 ml) and acetic anhydride (80 ml), stirred at room temperature, 20g N-neopentyl carbazole are introduced in a small portion. The reaction mixture is stirred at room temperature for an hour and then poured an ice-water. The yellow precipitate is filtered, washed with water until  $p^H=7$  and dried. The product is purified by repeated dissolution in THF and precipitation in water. The product is confirmed by checking the melting point and verifying the IR, NMR and UV spectra.



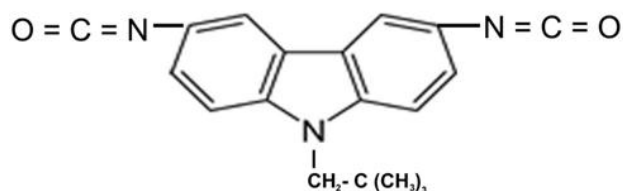
### 2.3. Preparation of 3, 6-Diamino N-neopentyl carbazole:

A mixture formed from 10g of dinitro compound, 56g of stannous chloride, 180 ml acetic acid and 30 ml concentrated hydrochloric acid are refluxed under nitrogen atmosphere for 25h. The initial yellow colour turns on after 1h reflux to orange and in time becomes brown. After 8h another portion of 10g stannous chloride and 5 ml concentrated hydrochloric acid are added. After 25h the reaction mixture is cooled and neutralized with sodium hydroxide solution (20%) and the pink precipitate is separated by filtration, washed with water and dried. It is purified by three times precipitation in water from acetone solution. The diamino compound is kept in dark and in nitrogen atmosphere. The diamino derivative is confirmed by checking the melting point and by IR, NMR and UV spectra.



### 2.4. Preparation of 3, 6-di-isocyanato N-neopentyl carbazole:

0.08 mols of phosgene mixed with toluene is taken in a three necked round bottom flask fitted with magnetic stirrer and a condenser. Then 0.04 mols of diamino compound with 100 cc. toluene is slowly added to the mixture. The mixture is stirred for 1h at room temperature. After that 0.2 mols of triethylamine is added to the reaction mixture and stirred vigorously. Then the reaction mixture is heated at  $100^{\circ}C$  for another 2h. After the reaction is over the mixture is cooled and precipitated out in hexane and washed with hexane and dried. The product is confirmed by checking the melting point and verifying IR, UV and NMR spectra. The product is kept in the dark and in nitrogen atmosphere.

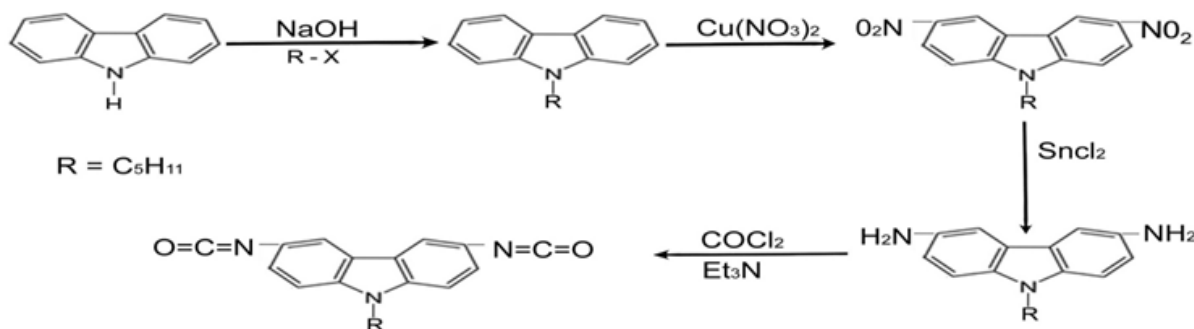


### 2.5 preparation of polymer:

0.04 mols of 3, 6-di-isocyanato N-neopentyl carbazole are dissolved in 100cc. of toluene. 0.04 mols of resorcinol or bisphenol-A mixed with toluene are slowly added to the reaction mixture and vigorously stirred at room temperature. The reaction mixture is stirred for 30 minutes at room temperature. After that the mixture is warmed at 50<sup>0</sup>c for another 1h. After the reaction is over the reaction mixture is cooled and precipitated out in methanol, washed with water and methanol and dried. The polyurethanes are characterized by IR, UV and NMR spectra.

### III. Result and Discussion:

The study of IR, NMR and UV spectra revealed the successful preparation of the polymers. The synthesis of carbazole based di-isocyanate monomer starting from carbazole is presented in detail in scheme-I.

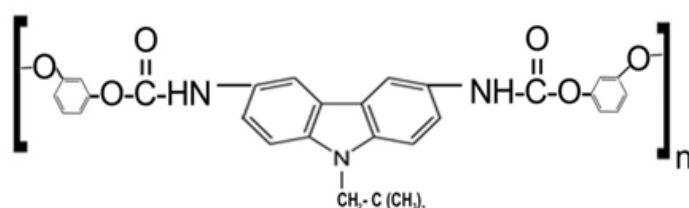


Scheme-I

N-neopentyl carbazole is prepared by treating carbazole with neopentyl bromide and solid sodium hydroxide in acetone. N-neopentyl carbazole is firstly dinitrated using copper (II) nitrate hemipentahydrate in a mixture of acetic acid and acetic anhydride. In the second step dinitro compound is reduced using stannous chloride in a mixture of concentrated hydrochloric acid and acetic acid at reflux temperature. A pure light pink coloured product in reasonable yields is obtained after three precipitations of acetone solution in water and the filtered solid product is dried and kept in dark and nitrogen atmosphere. The diamino compound is then treated with phosgene and triethylamine at first at room temperature and then heated at 100<sup>0</sup>c for several hours. The di-isocyanate derivative is precipitated out in hexane, washed with hexane and dried, and kept in dark and in nitrogen atmosphere.

The urethane polymers are synthesized by mixing equimolar quantities of 3, 6-di-isocyanate N-neopentyl carbazole and resorcinol or bisphenol-A. At first the reaction is carried out at room temperature for 30 minutes and then the mixture is warmed at 50<sup>0</sup>c for 1h. The reaction is carried out in organic solvent and polymers are separated with high yields by precipitation in methanol. The synthesized polymers are soluble in most common organic solvents. The substituted polyurethanes possess interesting electro-optical and photochemical properties as well as high thermal stability, mechanical strength and rigidity due to carbazole backbone.

Polymer of 3, 6-di-isocyanate N-neopentyl carbazole with resorcinol is given below as a typical example in scheme-II.



Scheme-II

#### **IV. Conclusion:**

This article has summarized the approaches to synthesize the monomer 3, 6-di-isocyanato N-neopentyl carbazole and the polymers with resorcinol and bisphenol-A. The polyurethanes possess many interesting properties like electro-luminescent property, electro-optical property. These polymers are finding many applications in xerography, photo-imaging and photo refractive materials. The most important polymers so far in commercial use is poly N-vinyl carbazole. However this polymer is quite costly and the preparation of the monomer is quite delicate. This investigation will help us to formulate a new and cheaper photo-conducting polymer. Moreover, these polymers can be studied for dark conductivity in sandwich configuration at different voltages; different temperatures with different sensitizers like TNF, crystal violet etc. same studies can be done under illumination at different wavelengths and different intensities.

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