Synthesis and characterization of a derivative of carbazole obtained from bromobenzyl alcohol

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Abstract. Carbazole and their derivatives are compounds that have a great importance in the industry because their potential applications in solid-state lighting technologies. These materials have photorefractive and photoconductive properties, it is charge transporter (hole) and it is employed in organic light emission diodes. Therefore, with the aim of to contribute in the art state of this type of materials was done the synthesis of a carbazole-based material, from carbazole and bromobenzyl alcohol, employing as catalyzer sodium hydroxide and as solvent sulfoxide dimethyl. The material obtained was characterized by hydroxyl value, infrared analysis, nuclear magnetic resonance, thermogravimetric, X ray diffraction and ultraviolet-visible analyses. By infrared and proton nuclear magnetic resonance analyses was evidenced the formation of the carbazole-based material. The carbazole-based material presented fluorescent properties, since when was taken to ultraviolet lamp, this material emitted light. The thermal stability exhibited by this material may facilitate its use under conditions of high temperature. The results obtained in this study are very important since so many fluorescent materials such as organic light emission diodes are doing imported in Colombia. Therefore, the carbazole-based material may be an alternative for substitution of importations of this type of materials.

1. Introduction

Carbazole (Cbz) is a material white crystalline, is a heterocyclic compound with a ring of five members containing nitrogen between two benzene rings. This material is thermally stable [1].

The Cbz nucleus is a heterocyclic structure present in a variety of compounds such as antimalarial, antitumor, antiplasmodial and antityrpanosomal activities [2]. Now day are doing synthesized so many compound derived from Cbz, since this material has photorefractive, photoconductive, hole-transporting and light-emitting properties [3].

Organic molecules type donator and acceptor are the conjugated organic materials more important. Compounds with donator and acceptor groups of electrons are connected through conjugated bonds (donator-π-acceptor). Thus, by employing different donators and acceptors of electrons may be obtained specific physical and chemical properties [4]. In the other hand, numerous species such as Cbz, fluorenes, thiofenes and oligothiofenes has been used as electron donators, but oxadiazols, diarylborons and quinolones has been employed as electron acceptors [4]. In these compounds, the donator mobility improves the hole injection and the transport. The great advantage of the Cbz is that present a good thermal and electrochemical stability [4].
The strategy usually employed for obtaining bipolar materials is the incorporation of the donator-acceptor in the same molecule, it facilities the transport of charge and electrons, it also may improve the emission efficiency since it probably increases the conjugation, but the same manner also to produce bathochromic effect which reduce the emission [5]. In comparison to other molecules, Cbz is used in the generation of absorptions and emissions at short wave length [5].

Cbz and its functionalized derivates in the positions 2, 7-3 and 6-9 have been frequently employed as luminescent materials in organic light emission diodes (OLEDs) due to its energy level of highest occupied molecular orbital (HOMO) and its capacity of charge transport [6]. So many derived from Cbz have been obtained, but they usually exhibit regular mechanical properties, low properties of film formation and quenching [6,7]. In the other hand, for the preparation of highly efficient OLEDs, is very important that the materials have a high glass transition temperature, uniform film morphology, good electrochemical stability and optic transparence that allow the step of the emitted light from mechanism, which ensures the high efficiency of light emission [8].

Thus, this study may increase the art state of these materials and could be employed for obtaining other fluorescent materials by modification of other compounds, such as hyperbranched polyesters for preparing fluorescent materials with nanometric hydrodynamic dimensions, which has not been reported. These materials may be also applied in coating industry, for example for obtaining fluorescent coating.

Cbz has been modified in the position 9 with some compounds such as cloroethanol [9], formaldehyde [10] and triazoles [11,12]. However, the modification of Cbz with bromobenzyl alcohol (ABrB) and the structural and thermal properties has been scarcely reported. Therefore, with the aim of to contribute in the art state of this type of materials was done the synthesis of 2-(9H-Cbz-9-y) benzyl alcohol (CbzA) from Cbz and ABrB, employing as catalyzer sodium hydroxide (NaOH) and as solvent sulfoxide dimethyl (DMSO). The material obtained was characterized by hydroxyl value (VOH), infrared analysis (IR), proton nuclear magnetic resonance ($^1$H NMR), thermogravimetric (TGA), X ray diffraction (DRX) and ultraviolet-visible (UV-Vis) analyses.

2. Materials and methods

The Cbz, ABrB, DMSO, NaOH, chloroform cetyl trimethyl ammonium bromide (CTAB) were supplied by Sigma Aldrich.

2.1. Preparation of the CbzA

In order to prepare the CbzA, the respective amount of Cbz (16.72 g) and NaOH (30 g) were taken to the reactor and then was added 100 mL of DMSO; the system was kept under nitrogen atmosphere, at 140 °C and a stir speed of 50 rpm. The system was allowed for reacting for one hour. Then were added the respective amount of CTAB (0.25 g) and the solution of ABrB in DMSO (28.06 g of ABrB dissolved in 50 mL of DMSO) and the system was kept reacting for 48 h, since this time is enough for obtaining the CbzA. Finally, the system was kept at room temperature, the product was extracted and precipitate in water and washed for removing the CTAB. Then the product (solid) of color brown was filtered. The solid was dissolved in chloroform and filtered. Then the solution resultant was mixed with water until complete precipitation of the solid. Finally, the solid (color brown-yellow) was dried at 50 °C. Figure 1 shows the schematic representation of the reaction between Cbz and ABrB.

![Figure 1. Schematic representation of the synthesis of CbzA.](image-url)
2.2. Characterization of the blends
In order to evaluate the fluorescence of the samples were prepared solutions of the Cbz, ABrB and CbzA 1.0 wt% in DMSO. These solutions were taken to a UV lamp and expose to UV light. VOH analysis was based in the standard method of the American Oil Chemists’ Society (AOCS) Cd 13-60 [1]. IR analysis was done in a Prestige 21 spectrometer of Shimadzu using 8 scans and a resolution of 4 cm⁻¹. For it were prepared pills of the samples by using potassium bromide. ¹H NMR analysis was performed in a Bruker AC 300 MHz spectrometer to a solution of CbzA 1.0 wt% in deuterated chloroform. The TGA analysis was executed in a TA Instruments SDT Q600 equipment using a heating rate of 20 °C/min. from room temperature until 600 °C employing a purge of nitrogen. The DRX analysis was performed in a PANalytical X’Pert PRO MPD diffractometer by using a radiation of Cu Kα=1.5406 A. The current and the voltage were 40 mA and 45 kV respectively.

3. Results and discussion
Figure 2 shows the photo of the solution of CbzA submitted to UV light. It can be observed that the sample CbzA presented fluorescence and the emitted light is color yellow. This result is very important since it allow evidencing that was obtained a fluorescent material.

![Figure 2. Picture of the solutions of CbzA exposed to UV light.](image)

The CbzA exhibited a VOH of 67.95 mg KOH/g sample, this mean that the reaction between Cbz and ABrB was carried out. Figure 3 shows the IR spectra of the Cbz, ABrB and CbzA. It can be seen that ABrB presents a signal at 800 cm⁻¹, which is due to stretching of C-Br bond. The overtone around 1800 cm⁻¹ is due to vibrations of aromatic carbons. At 3330 cm⁻¹ appears a signal corresponding to stretching OH groups. Cbz exhibited the same overtones that ABrB, but also show a signal at 3409 cm⁻¹ which corresponds to stretching of N-H bond. This signal and that of the C-Br not appeared in the CbzA spectrum, it means that was carried out the reaction between Cbz and ABrB.

The ¹H NMR spectrum (Figure 4) shows different shift (δ), which are assigned as follow: at 7.89 ppm and 8.34 ppm appear a multiplete due to protons of C₄ and C₅, between 6.63 ppm and 7.79 ppm is observed another multiplete which is associated with others carbon atoms presents into the aromatic structure of the CbzA. The signal at 4.57 ppm is attributed to protons of methylene carbons join to OH groups (-CH₂-OH), the signal that appears at 3.79 ppm (singlete) is due to the proton of OH. The signals that appear between 1.0 ppm and 2.0 ppm are probably associated with CTAB, since despite of the purification process this material remained in the sample. The absence of the signals due to N-H bond in the CbzA spectra (IR and ¹H NMR) is a proof of the formation of this compound. It also was observed to the 9,10-diphenylanthracene containing 9H-Cbz derivatives [13].

The difractogram of the Cbz is presented in Figure 5 and that of the CbzA is showed in Figure 6. Cbz exhibited various peaks which appear at 2θ values: 10.46°, 21.40°, 22.92°, 27.02°, 32.64°, 36.44°, 42.37°, 44.49° and 55.29°. It means that this material is crystalline. Some of these values already have been reported for Cbz [14] and its crystalline arrange is orthorhombic [15]. In addition, CbzA (Figure 6) presented a small peak between 2θ=5° and 2θ=15° and 2θ=22.92° and 2θ=32.64°. These peaks exhibited a negligible intensity, which can be seen in the intensity values of the peaks observed to Cbz respect to those of the CbzA. The DRX result indicates that the Cbz lost great part of its crystallinity during the reaction with ABrB, since the sample CbzA is mainly amorphous. In a study of the physical and structural properties of biofield energy treated Cbz were observed very sharp and intense peaks [16].
Figure 3. IR spectra of the samples.

Figure 4. $^1$H NMR spectrum of the CbzA.

Figure 5. Diffractogram of the Cbz.

Figure 6. Diffractogram of the CbzA.

Figure 7. TGA thermograms of the samples. The decomposition temperatures of the samples when has been degraded 5 wt% are the followings: ABrB: 144 °C, Cbz: 233 °C, CbzA: 114 °C. It can be observed that initially the ABrB and Cbz present higher thermal stability than the sample CbzA, but around 300 °C the samples ABrB and Cbz experimented a thermal decomposition higher than 95%. However, the sample CbzA at 600 °C exhibited a residue of 14.19 wt%. This means that this sample has a highest thermal decomposition. This behavior may be due to presence of compounds of high thermal stability (sample CbzA), which were formed during the heating process, the same has been reported by other authors [16]. Figure 8 shows the UV spectrum of the sample CbzA. This sample presented an absorption in the UV region. The wave length in the maximum of absorption was 330 nm. This result allows evidencing once more that the CbzA has fluorescent properties. In a study of the synthesis of Cbz-based material were observed two peaks at 329 nm and 340 nm attributed to $\pi\rightarrow\pi^*$ transitions of the Cbz moiety [17].

Figure 7. TGA thermograms of the samples.

Figure 8. UV spectrum of the sample CbzA.
4. Conclusions
In this study was prepared a derivative of Cbz (CbzA). This material presented fluorescent properties, since when was taken to UV lamp this material emitted light. The CbzA presented highest residue after thermal treatment, which was due to possibly was carried out a chemical reaction during this process. By DRX analysis was determined that the sample CbzA is mainly amorphous and the Cbz is crystalline. By UV-Vis spectroscopy was evidenced the absorption of the sample CbzA in the range of wave length between 300 nm and 350 nm. Therefore, CbzA may be an alternative for being used as fluorescent material in some applications, since is the same range of wave length that presenting usually the fluorescent materials employed in several applications (OLEDS, dyes, etc).

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