

Synthesis and Characterization of tris-(4-Phenoxyphenyl)amine by Conventional Method

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Abstract: Conjugated and non-conjugated compounds were synthesized. The compounds were synthesized by two step reaction *i.e.* (1) by direct bromination of the organic compound followed by N/O-alkyl/arylation and (2) by bromomethylation of the organic compound followed by N/O-alkyl/arylation.

Keywords: Synthesis, Organic electroluminescence, Conjugated, Non-conjugated compounds

Introduction

Organic electroluminescence (EL) is the electrically driven emission of light from non-crystalline organic materials, which was first observed and extensively studied in the 1960s^{1,2}. In 1987, a research group in Kodak introduced a double layer organic light-emitting diodes (OLEDs), which combined modern thin film deposition techniques with suitable materials and structure to give moderately low bias voltages and attractive luminance efficiency^{3,4}. Later in 1990 the Cambridge Group of Friend announced the first conducting polymer-based LED^{5,6}. Since after that, there have been tremendous research activities in this new field and enormous progress have been made in the improvements of color gamut, luminance efficiency and device reliability. The growing interest is largely motivated by the promise of the use of this technology toward full-color flat panel displays.

The amorphous nature of the TPA containing materials can be enhanced by the attachment of bulky substituents or the generation of more extended TPA oligomers via connection by para-linkages. The star shaped triphenylamine structures leads to a decreased crystallization tendency due to bulky, non polar geometry. Synthesized number of low oxidation potential star-shaped oligo triarylamine compounds with different cores (Figure 1).

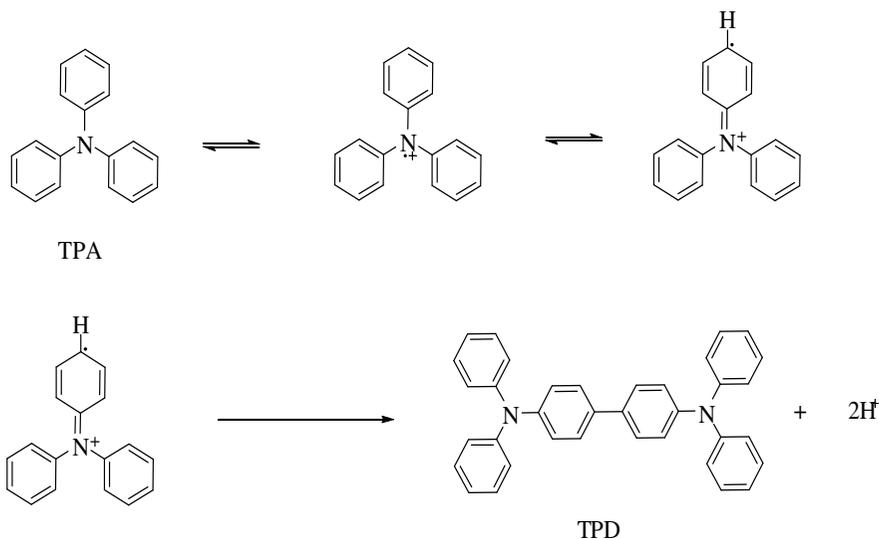


Figure 1. Dimerization of the cationic triphenylamine (TPA) moiety

Experimental

Triphenylamine was purchased from Sigma Aldrich India, bromine, phenol, 18-crown-6-ether, potassium carbonate were purchased from Spectrochem chemicals India Pvt. Ltd. The solvents were distilled off and dried by the conventional known methods before their use.

Characterization

¹H NMR and ¹³C NMR were recorded on JEOL-400MHz NMR in the University Science Instrumentation Centre (USIC), Faculty of Science, University of Delhi. FT-IR was recorded on Perkin Elmer FT-IR spectrometer from the Department of Chemistry, University of Delhi. The UV-Vis absorption spectrum was recorded by Shimadzu UV spectrophotometer and the fluorescence spectra was recorded by Cary Eclipse fluorescence spectrophotometer from University Science Instrumentation Centre (USIC), Faculty of Science, University of Delhi.

Synthesis⁷ of tris-(4-bromophenyl)amine

Triphenylamine (1.2 g, 5 mmol) was dissolved in 5 mL of chloroform and cooled down to 0 °C. After half hour bromine (0.5 mL dissolved in 3 mL chloroform, 20 mmol) was added to the reaction mixture and the resulting green solution was stirred for another one hour. The reaction mixture was poured in 20 mL (1:1) ethanol:water mixture to precipitate out the product. The solid was filtered off under vacuum and dissolved in 4 mL hot chloroform. After addition of 15 mL hot ethanol the product was allowed to crystalline over night at -18 °C. The synthesis of the organic compound was confirmed with melting point 142 °C and ¹H NMR shown in Figure 2.

Synthesis of tris-(4-phenoxyphenyl)amine

Tris-(4-bromophenyl)amine (1 g, 2 mmol), phenol (0.6 mL, 6 mmol), 18-crown-6-ether (1.5 g) and K₂CO₃ (1 g) were dissolved in 10 mL acetone and allowed to reflux at 50 °C for 60 h (Scheme 1). The reaction progress was monitored by TLC in hexane : ethyl acetate (70:30%). After this the reaction was quenched by adding 100 mL distilled water and organic compound was extracted using chloroform (4x50 mL). The organic layer was dried over sodium sulfate and the solvent was removed under rotavapor. The compound was purified by column

chromatography (Hexane: Ethyl acetate, 80:20) and pale yellow colored solid with melting point 129 °C was obtained. The compound was further confirmed by and ^1H NMR and ^{13}C NMR shown in Figure 3 & 4.

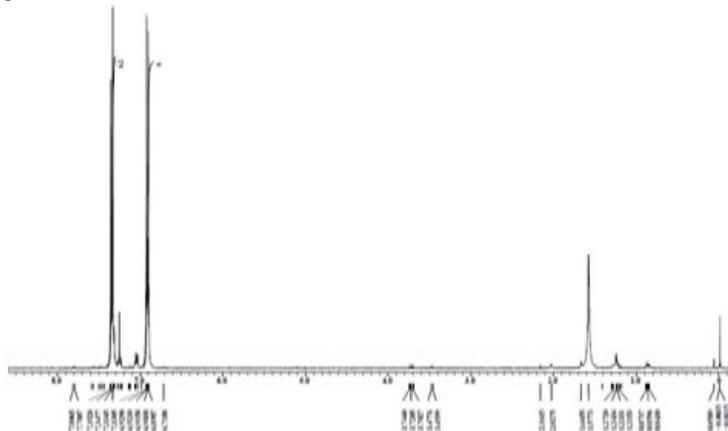
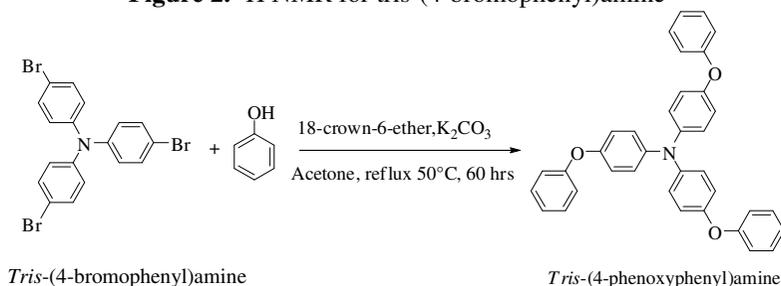


Figure 2. ^1H NMR for tris-(4-bromophenyl)amine



Scheme 1

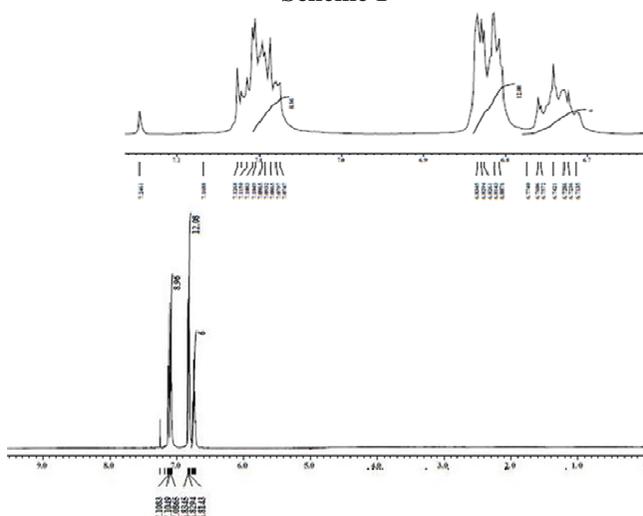


Figure 3. ^1H NMR for tris-(4-phenoxyphenyl)amine

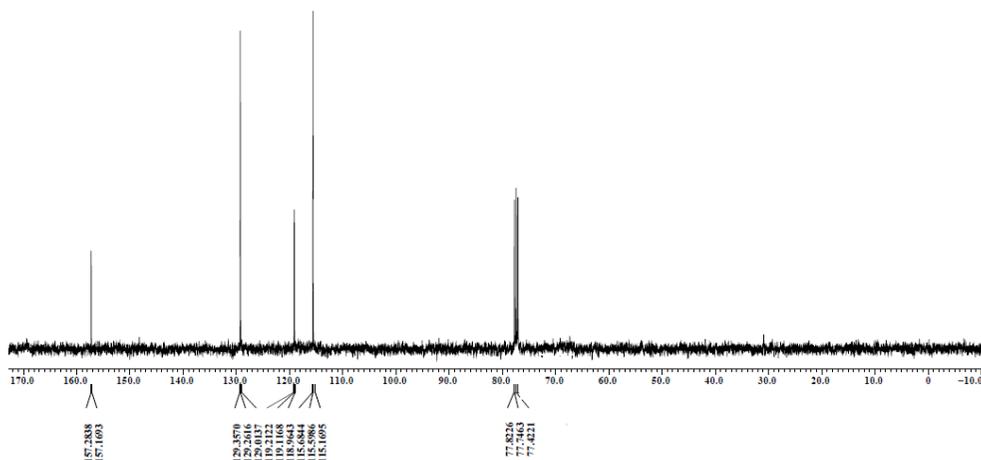


Figure 4. ^{13}C -NMR for tris-(4-phenoxyphenyl)amine

^1H NMR (400 MHz CDCl_3 , δ , ppm) for tris-(4-phenoxyphenyl)amine in Figure 3 shows the peak at 6.7135-6.7748(6 H) which corresponds to the protons of the triphenylamine, the peak at 6.8143-6.8345(12 H) corresponds to the proton of the aryl ring attached with the ethereal linkage, and the peak at 7.0866-7.1063(9 H) is for the peripheral protons of the aryl ring. Similarly ^{13}C NMR (400 MHz CDCl_3 , δ , ppm) shown in Figure 4 represented all the carbon of the aryl ring at 157.28, 157.16, 129.35, 119.21 and 112.68.

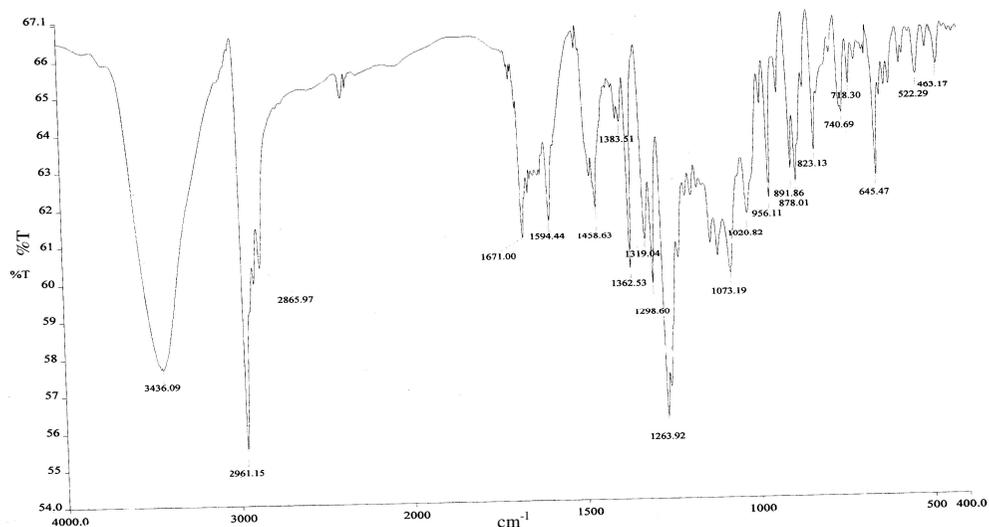


Figure 5. FT-IR spectra of tris-(4-phenoxyphenyl)amine

FT-IR spectra for the tris-(4-phenoxyphenyl)amine (Figure 5) was recorded in KBr as the medium. The stretching at 1020.82 cm^{-1} corresponds for $-\text{C}-\text{N}$ bond and stretching peak at 1073.19 for the $-\text{C}-\text{O}$ ethereal linkage, the peak at 1362.53 cm^{-1} is for $\text{C}=\text{C}$ of the aromatic ring and 2965 cm^{-1} for the CH -of the aromatic ring. The broad peak at 3436.09 cm^{-1} was observed due to the presence of water in the medium of the spectra.

The UV-Visible spectra for tris-(4-phenoxyphenyl)amine (Figure 6A) was recorded in tetrahydrofuran (THF) and shows a good maximum absorption (λ_{max} 308 nm) with an absorption of 1.408. The florescence for the tris-(4-phenoxyphenyl)amine (Figure 6B) was also recorded in tetrahydrofuran (THF) and gave a good emission (λ_{max} 410 nm) with intensity of 72.54 a.u.

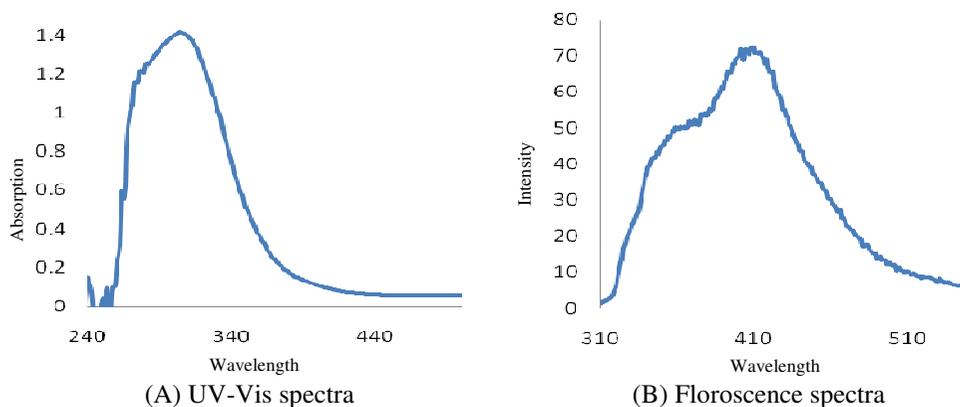


Figure 6. UV-Vis and florescence spectra of tris-(4-phenoxyphenyl)amine

Results and Discussion

In this paper, the synthesis of triphenylamine based compounds with reaction between tris-(4-bromophenyl)amine and phenolic compounds like phenol and naphthol is reported. The synthesized compounds were characterized and confirmed by ^1H NMR, ^{13}C NMR, FT-IR, UV-Vis. spectroscopy and florescence spectroscopy. In this paper tris-(4-phenoxyphenyl) amine, the tris-(4-bromophenyl)amine undergoes electrophillic substitution reaction with the nucleophile generated from the phenol by cleavage of the phenolic -OH bond. The study reveals that the lone pair of electrons in the ethereal linkage makes the energy increased and hence decrease in absorption towards lower wavelength. The synthesized compound and their derivatives will be used for biological and other applications.

Acknowledgement

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