

- I. Stereochemistry of the stepwise oxidation of *tris*[4-propylthiophenyl]amine
- II. Synthesis of Triphenylamine Electrocatalysts:
Nitration of *tris*[4-propylsulfonylphenyl]amine

by

Ernest I. Sliwinski
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TABLE OF CONTENTS

Acknowledgments.....	3
Abstract.....	4
I. Stereochemistry of the stepwise oxidation of <i>tris</i> [4-propylthiophenyl]amine	
Introduction.....	7
A. Stereochemistry at the sulfur center.....	7
B. Stereochemical analysis using NMR spectroscopy.....	10
C. Oxidation of sulfides.....	12
Synthesis.....	14
Results.....	31
Discussion.....	33
Experimental.....	40
References.....	43
II. Synthesis of Triphenylamine Electrocatalysts: Nitration of <i>tris</i> [4-propylsulfonylphenyl]amine	
Introduction.....	45
Synthesis.....	51
A. Preparation of <i>tris</i> [4-propylsulfonylphenyl]amine.....	51
B. Nitration of <i>tris</i> [4-propylsulfonylphenyl]amine.....	52
Results and Discussion.....	60
A. Cyclic voltammetry.....	60
B. Potential catalytic applications.....	63
C. Synthetic considerations.....	65
Experimental.....	68
References.....	72

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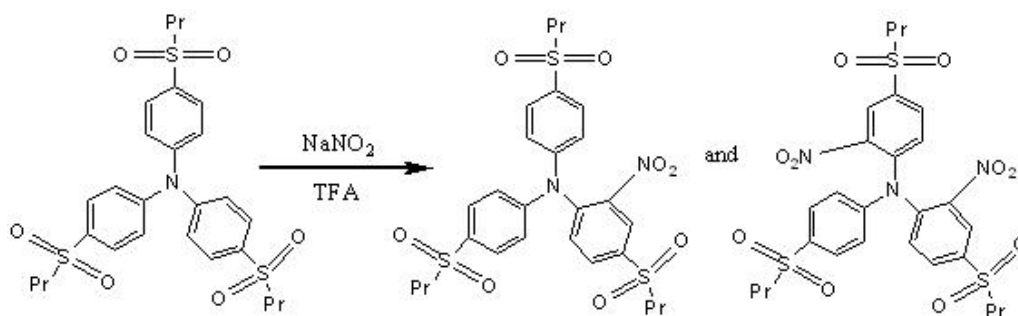
ABSTRACT

I. Stereochemistry of the stepwise oxidation of *tris*[4-propylthiophenyl]amine

The study of stereochemistry present at sulfoxide centers has been studied in the past, but has not been done on a more complex system such as that involving propylsulfoxyl-containing triphenylamines. The goal of the study was to determine the number of different stereoisomers present in each step of the oxidation. The synthesis of sequentially oxidized *tris*[4-alkylthiophenyl]amine was completed in reactions by varying the stoichiometric amounts of *m*-chloroperoxybenzoic acid in CH₂Cl₂. Stereochemical analysis with the use of ¹³C NMR or ¹H NMR spectroscopy was not effective as different stereoisomers were not resolved in the spectra attained. Analysis utilizing lanthanide chiral shift reagents was only initially performed on *tris*[4-propylsulfoxylphenyl]amine (**4**) using Eu(tfc). Although not obtained reproducibly, a ¹H NMR spectrum was obtained that does indeed show the presence of different stereoisomers in the 4,4',4''-tripropylsulfoxyltriphenylamine (**4**) and suggests that the expected mixture of diastereomers was produced and can be studied further with success, although the optimal conditions for such discrimination may be very specific and difficult to determine. Future work will have to closely study which solvent, lanthanide shift reagent, concentration of shift reagent, temperature and other conditions consistently result in spectra that resolve the stereochemistry of all the step-oxidized compounds.

II. Synthesis of Triphenylamine Electrochemicals: Nitration of *tris*[4-propylsulfonylphenyl]amine

High oxidation potential triphenylamine electrocatalysts are employed to oxidatively cleave stilbenes bearing electron withdrawing groups by electrocatalytic anodic oxidation in aqueous acetonitrile. In previous literature, it has been reported that 4,4',4''-tribromotriphenylamine is a good electrocatalyst for the oxidation of compounds with very low potentials. A better electrocatalyst would be desirable in order to oxidize compounds with much higher oxidation potentials bearing electron withdrawing groups. Using a method reported by Uemura and coworkers, successful nitration of *tris*[propylsulfonylphenyl]amine was carried out with sodium nitrate in trifluoroacetic acid. With the control of stoichiometric amounts of sodium nitrate, either the mono-nitrated or di-nitrated species can be obtained. Purification was achieved using flash chromatography and recrystallization. Cyclic voltammetry experiments were carried out to measure the oxidation potential of these compounds. Future work will involve the use of these catalysts in electrolysis experiments to measure their effectiveness.



I. Stereochemistry of the stepwise oxidation of *tris*[4-propylthiophenyl]amine

INTRODUCTION

A. Stereochemistry at the sulfur center

Sulfur has been studied as a stereogenic center for more than a century.^{1,2} At first, sulfonium salts were studied $(R^1R^2R^3S)^+X^-$, where X is a halogen and the R groups are different from each other. As determined by X-ray crystallography, this ion has pyramidal geometry with a lone pair of electrons. The pyramidal structure is capable of atomic inversion to form enantiomeric, mirror-image structures, through a planar transition state and with a 25-29 kcal/mol energy barrier. This same configuration is also observed in sulfoxides (R_1R_2SO) where the inversion barrier is 35-43 kcal/mol where stable enantiomers are observed if R_1 and R_2 are different.¹

The sulfur-oxygen bond in sulfoxides is of interest as it differs greatly from a carbon-oxygen π -bond. In the sulfoxide bond, electrons from the lone pairs of oxygen are contributed to the d orbital of sulfur resulting in an overlap of the sulfur d orbital with a p orbital of the oxygen. The best representation of the partial double bond is represented below with two resonance structures (Fig. 1).¹

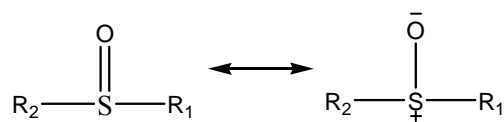


Figure 1 – Possible resonance structures for sulfoxides (R_1R_2SO)

The sulfone, $R_1R_2SO_2$, geometry is believed to resemble a regular tetrahedron. In sulfones, there are four possible resonance structures represented on the next page (Fig. 2). Here, there are two electron pairs that may overlap with the sulfur d orbitals. The major contributors to the structure are likely the two middle resonances as they

acknowledge the differences in electronegativity of sulfur and oxygen, but also do not have too much charge separation as does the rightmost one.¹

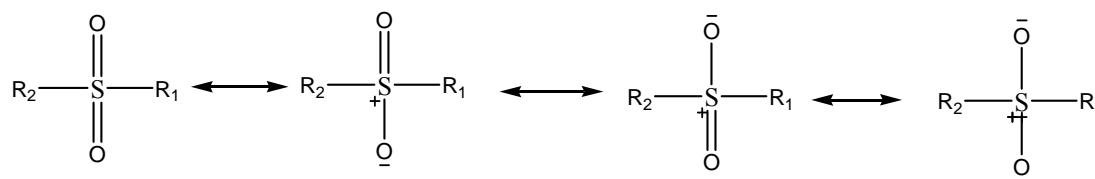


Figure 2 – The possible resonance structures for $R_1R_2SO_2$

For the purposes of denoting different enantiomers, the Cahn-Ingold-Prelog system is employed with R and S.³ It is stated that “contributions by d orbitals to bonds of quadrivalent atoms are neglected,” meaning that the sulfur-oxygen bond is considered a single bond.³

A number of studies have been performed studying chirality at sulfur atoms in organic compounds.^{4,5,6} It would be of interest, however, to study the stereochemistry of a more complex system. The 4,4',4''-tripropanethiotriphenylamine (**1**) compound can be oxidized in a step-wise fashion by a number of methods described later. The oxidation of that thiol to the sulfone has been reported earlier. The corresponding oxidized compounds ranging from the sulfide to the sulfoxide to the sulfone will then be extracted and purified. As there are three places where the oxidation can occur, a total of five compounds will be studied (**2-6**). The desired compounds (**2-6**) to be synthesized are shown on the next page (Fig. 3).

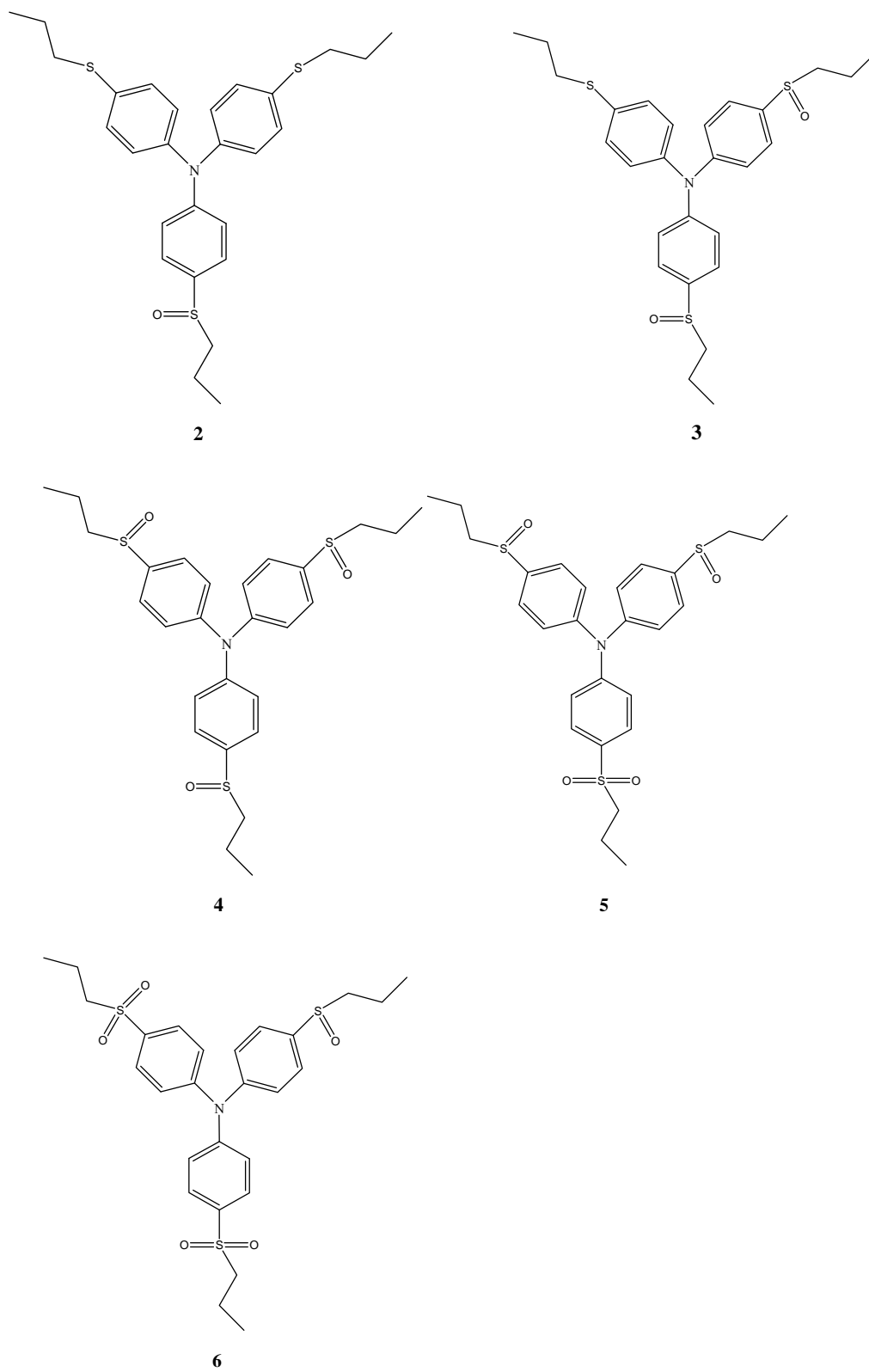


Figure 3 – Products of the step-oxidation (2-6) of *tris*[4-propylthiophenyl]amine (1).

B. Stereochemical Analysis Using NMR Spectroscopy

The first approach to the determination of the stereoisomers present in the each compound will be to attain ^{13}C NMR spectra. This NMR method has been previously shown to discriminate between the different stereoisomers in compounds where the stereocenter is not only carbon, but also sulfur.⁷ Studies involving the use of ^{13}C NMR to show the stereochemistry of a number of compounds have been completed with success.⁸

To resolve the different chiral compounds and show the number of different stereoisomers that exist of each oxidized compound, chiral shift reagents can also be utilized in ^1H NMR spectroscopy. The association of these optically active reagents with a chiral center leads to the formation of nonequivalent diastereomeric complexes. These complexes lead to distinct resonances in an NMR spectrum, since complexed nuclei are no longer equivalent. Chiral derivatizing agents form a covalent bond with the substrate to be analyzed, while solvating chiral reagents associate with the substrate through noncovalent interactions arising from dipole-dipole, ion-pairing, and/or π - π interactions.⁹

For the resolution of sulfur chiral centers, solvating agents are suggested.⁹ The choice of the solvent is a very important aspect of the use of these reagents. Steric effects are also an important consideration for the recognition of different stereoisomers. These shift reagents are known to exchange with substrates quickly and the observed NMR spectrum is the average of the bound and unbound substrate. If the exchange occurs slowly and there is some enantiomeric specificity, three resonances are observed, where one refers to the unbound substrate, one to the R and

one to the S isomers. An intermediate rate of exchange results in broader peaks, so fast exchange is desired to cleanly resolve the different stereoisomers. Enantiomeric discrimination is both temperature and concentration dependent.⁹

Paramagnetic lanthanide complexes, usually hard Lewis acids, are commonly used as chiral shift reagents that complex with hard Lewis bases. These reagents have been used widely for organic compounds, as they will complex with functional groups containing oxygen, nitrogen, and even those that contain sulfur, which are regarded as softer Lewis acids.⁴ Line broadening due to paramagnetic ions has been reported.⁹ The use of lanthanum(III), lutetium(III), samarium(III), and europium (III) complex (Fig. 4) with trifluoro camphorate (tfc) and heptafluoro camphorate (III) has been reported.⁴ Due to the electron-withdrawing nature of fluorine, the chelates formed by tfc and hfc result in a more positive lanthanide ion, allowing it to complex with donor substrates. It has been found that neither tfc nor hfc consistently cause better chiral discrimination and there appears to be no way to predict which works better for a particular substrate.^{9,10} Trisdipivalomethanatoeuropium(III) has been previously used to resolve sulfoxides successfully.⁵

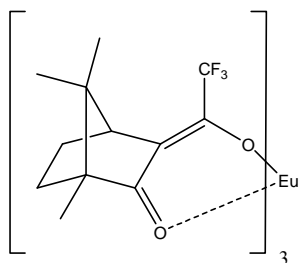


Figure 4 - Europium tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorate] abbreviated by Eu(tfc).

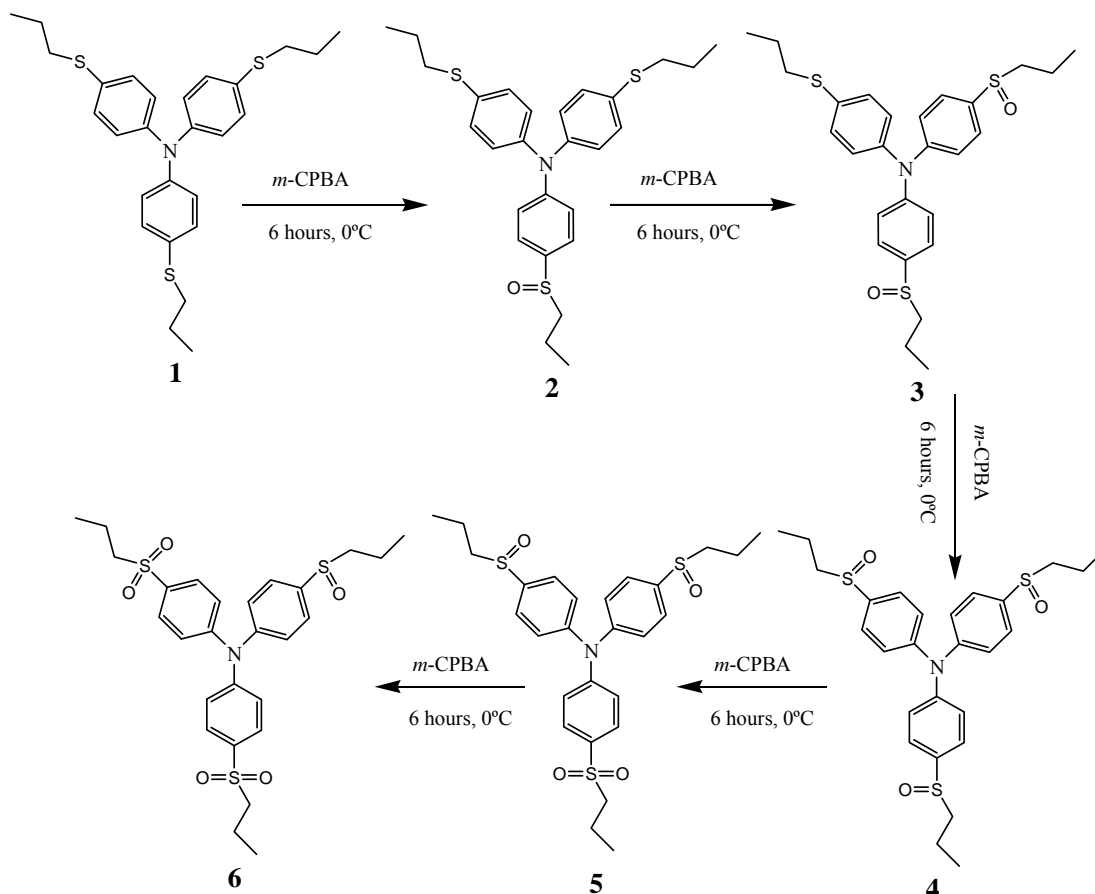
The use of lanthanide shift reagents has been noted for methyl phenyl sulfoxide, which is very similar to the triphenylamine thiol compounds investigated here.⁴ The broadening of the methyl resonances was so strong as to not allow for enantiomeric discrimination. The study of the vinyl group of phenyl vinyl sulfoxide suggested that there is a mix of shielding and deshielding effects along with each complex. These studies led to the conclusion that there is no correlation between the amount of enantiomeric discrimination in the spectra and the magnitude of the complexation shifts.⁴

C. Oxidation of Sulfides

The oxidation of 4,4',4''-tripropylthiotriphenylamine (**1**) has previously been reported with the use of the KHSO₅, commercially available as OXONE®, resulting in 4,4',4''-tripropylsulfonyltriphenylamine (**7**).¹¹ The OXONE® reagent, however, is quite potent and fully oxidizes the sulfide to the corresponding sulfone very quickly. Hence, it would be difficult to synthesize and isolate the compounds oxidized step by step. A number of more mild reagents are available for the oxidation of sulfides to sulfoxides and later to sulfones. *m*-chloroperoxybenzoic acid (*m*-CPBA) is a common reagent used for the oxidation of sulfides.¹² This reagent, however, has been reported to necessitate the strict use of low temperatures (to even below -30°C), be only partially soluble in dichloromethane, and be difficult to separate from the sulfoxides. Despite these limitations, the availability of the reagent and its appropriate level of potency make it a strong candidate for this transformation.¹² Other efficient methods of oxidizing sulfides include utilizing the surface of silica, alumina, and K10.¹³ It has been reported that the use of silica gel mediates the oxidation of sulfides and prevents

over-oxidation.¹³ Methods which utilize solid support for the oxidation include $\text{H}_2\text{O}_2/\text{SiO}_2/\text{Ac}_2\text{O}$,¹⁴ $t\text{-BuOOH}/\text{SiO}_2$,¹⁵ and $\text{OXONE}/\text{SiO}_2$.¹⁶ The absence of overoxidation has also been reported in the use of $\text{KF}/m\text{-CPBA}$ in the conversion of sulfides to sulfoxides.¹⁷

SYNTHESIS



The synthesis of compounds **2** – **6** was completed using *m*-CPBA on the starting material *tris*[4-propylthiophenyl]amine (**1**). By controlling the stoichiometric amounts of the oxidizing reagent, any of the compounds can be attained from the reaction in sufficient yield in an approximately six hour reaction at 0°C. The separation of each compound is done through the use of flash chromatography with a 10% methanol / 90% ethyl acetate solution as the mobile phase. No attempts were made at developing a reaction that would maximize the yield of each compound, as only analytical amounts of each one was desired. The reaction does need to be run on ice as to maintain the stability of the reactive peroxide. Earlier attempts of performing

this reaction at room temperature failed. After flash column chromatography, compounds **2** – **6** are oils, despite appearing pure through thin layer chromatography and ^1H NMR spectroscopy. Trituration in hexanes at around -78°C results in crystals.

4,4'-dipropylthio-4''-monopropylsulfoxyltriphenylamine (**2**)

^1H NMR of **2** is shown on the next page (Fig. 5) and is characteristic of the assigned structure. There are four aromatic resonances, each one a doublet as expected. Two large resonances corresponding to 4H each have shifts indicative of the thiol species (**1**) at 7.03 and 7.29 ppm. Two small resonances integrating to 2H are shifted a bit downfield to around by approximately 7.46 and 7.07 ppm. The downfield shift due to the sulfoxide is expected due to the presence of the oxygen. A major downfield shift for the aromatic resonances has also been noted previously in the oxidation of this thiol to the sulfone.¹¹ In the alkyl region of the spectrum, the methyl integrating to 9H is noted as a triplet and the middle methylene is noted to integrate to 6H as a multiplet as expected. The methylene bonded to the sulfur is split into two triplets with a ratio of 4H to 2H. This initially appeared inconsistent with the shift of the aromatic resonances, as the sulfoxide would be expected to shift the alkyl protons downfield rather than upfield in relation to the unoxidized thiol.

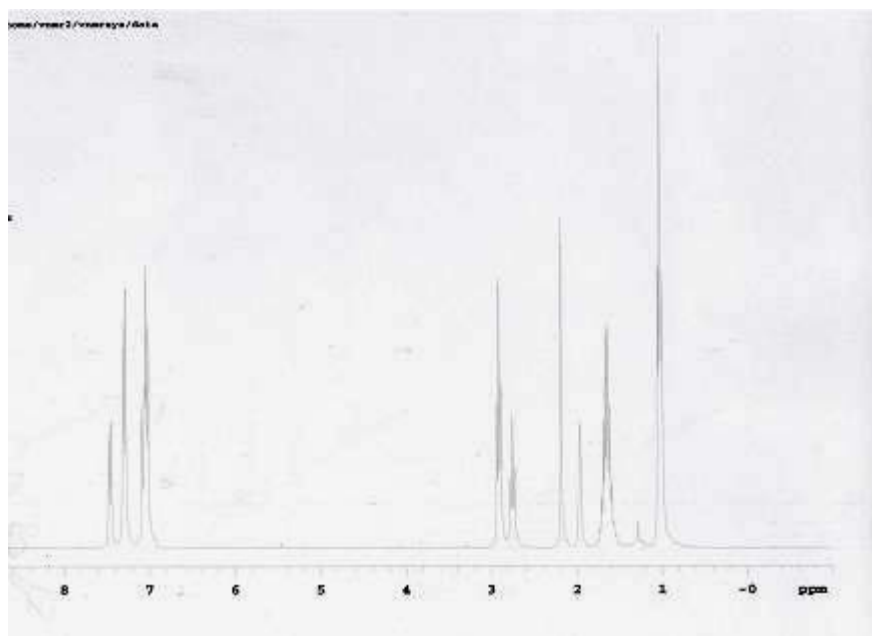


Figure 5 - ^1H NMR of 4,4'-dipropylthio-4''-monopropylsulfoxyltriphenylamine (2)

4,4'-dipropylthio-4''-monopropylsulfoxyltriphenylamine (**2**)

^{13}C NMR spectrum of **2** is shown below (Fig. 6) and agrees with the assigned structure. There are 6 carbons in the alkyl region with three corresponding to the sulfoxide chain and the other three to the thiol chain. The aromatic region shows 8 carbons, which is consistent with the expectation of four carbons belonging to the sulfoxyl-substituted ring and the other four belonging to the thio-substituted rings.

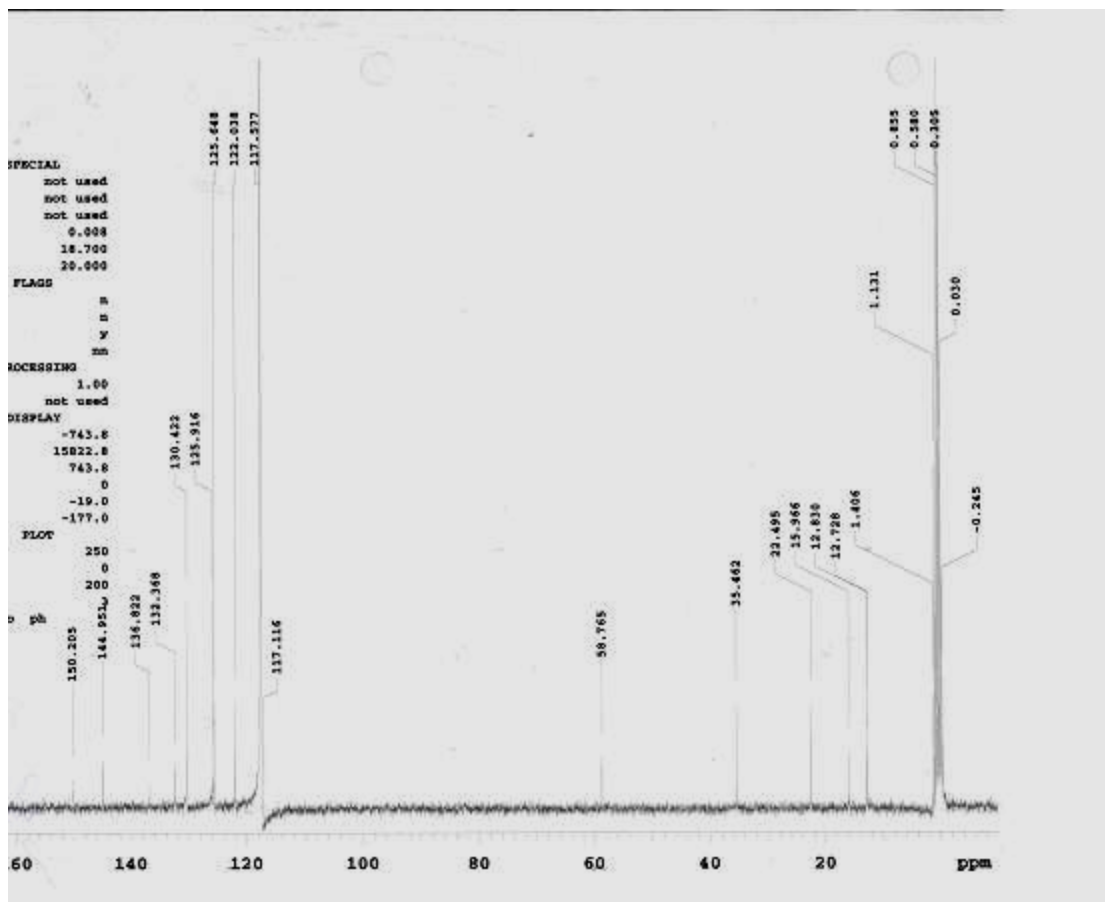


Figure 6 – ^{13}C NMR of 4,4'-dipropylthio-4''-monopropylsulfoxyltriphenylamine (**2**)

4,4'-dipropylthio-4''-monopropylsulfoxyltriphenylamine (**2**)

The COSY NMR shown below (Fig. 7) further confirms the structure of **2**. The small aromatic resonances corresponding to the sulfoxyl-substituted ring are coupled with each other. The thiol resonances are coupled to each other as well. All the alkyl protons also consistently couple with their vicinal neighbors.

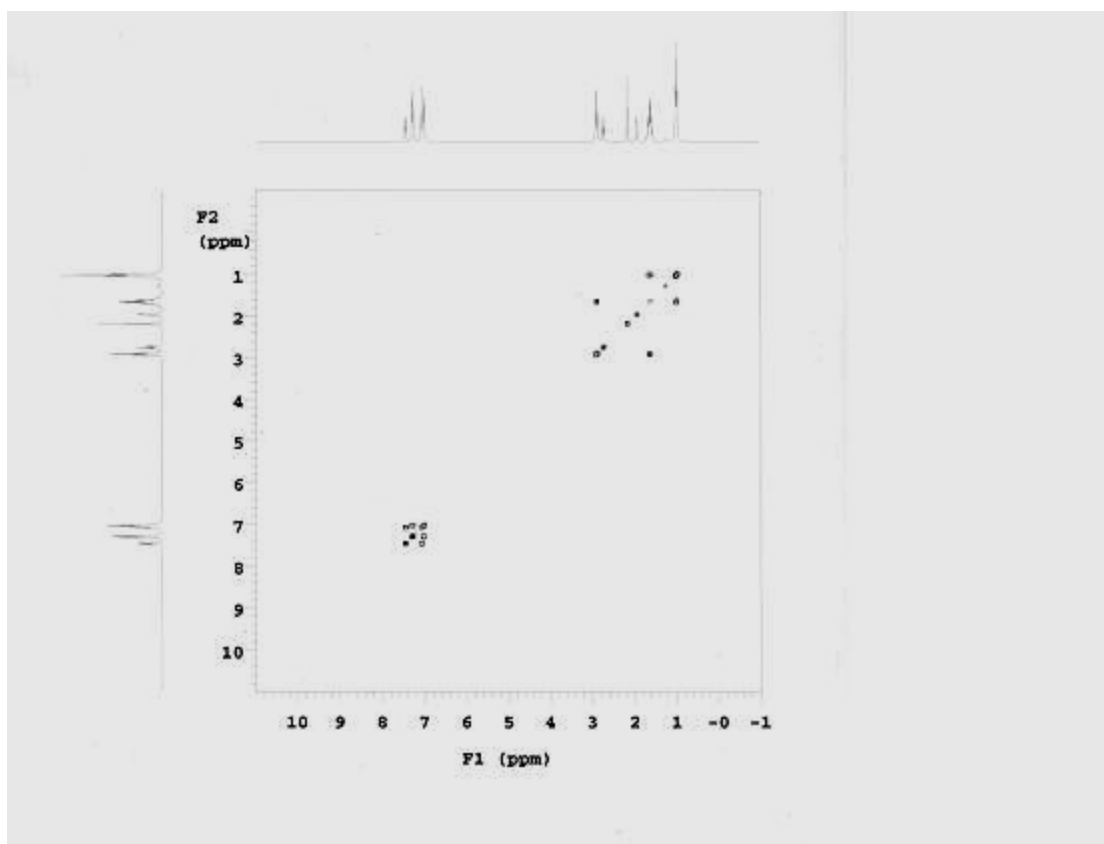


Figure 7 - COSY NMR of 4,4'-dipropylthio-4''-monopropylsulfoxyltriphenylamine (**2**)

4-monopropylthio-4',4''-dipropylsulfoxyltriphenylamine (**3**)

^1H NMR of **3** is shown below (Fig. 8) and is consistent with the ^1H spectrum of **2**, except those peaks that were identified to correspond with the sulfoxyl-substituted ring are now integrating in a 2:1 ratio with those that were identified with the thio-substituted ring, as expected. A slightly more downfield shift for all resonances is noted in this compound as compared to **2**.

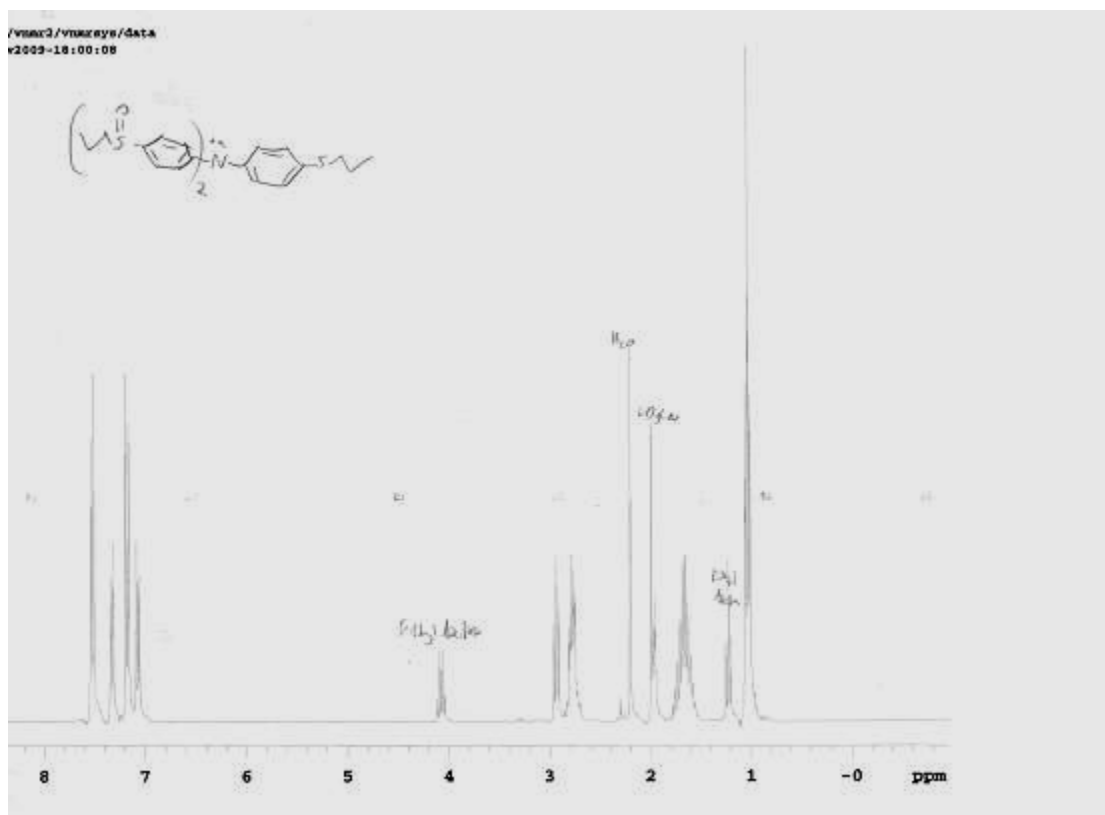


Figure 8 - ^1H NMR spectrum of 4-monopropylthio-4',4''-dipropylsulfoxyltriphenylamine (**3**)

4-monopropylthio-4',4''-dipropylsulfoxyltriphenylamine (**3**)

^{13}C NMR spectrum of **3** is shown below (Fig. 9) and although it was taken with fewer scans, it also appears consistent with the spectrum of **2**, as expected. The chemical shift in the spectra for **2** and **3** are also very similar.

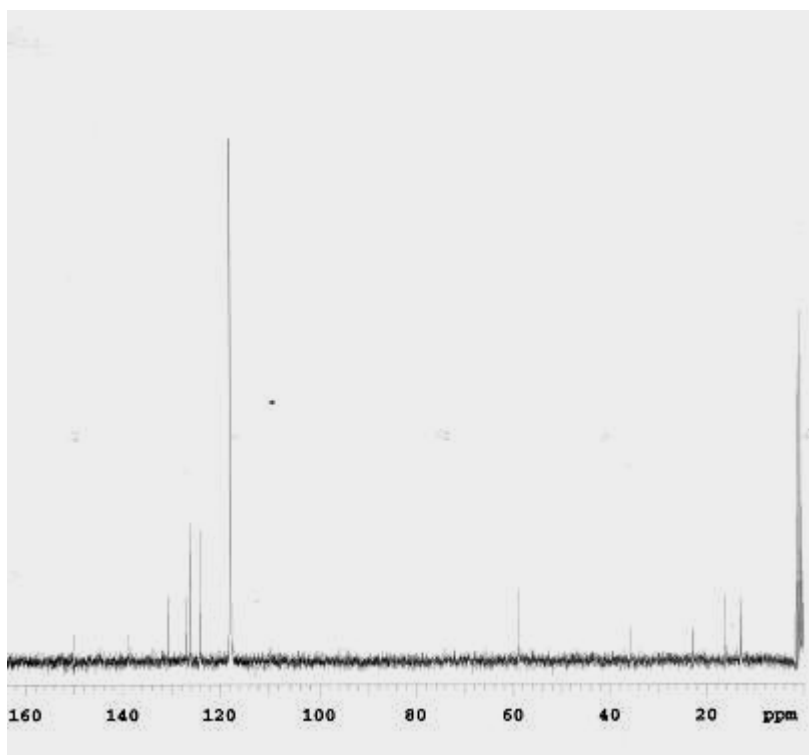


Figure 9 – ^{13}C NMR spectrum of 4-monopropylthio-4',4''-dipropylsulfoxyltriphenylamine (**3**)

4-monopropylthio-4',4''-dipropylsulfoxyltriphenylamine (**3**)

COSY NMR of **3** is shown below (Fig. 10) and further suggests that the isolated compound is in fact **3**. The alkyl protons all couple with their vicinal neighbors, as well as the aromatic protons, which couple with others on the same ring. The two aromatic protons on the sulfoxyl-substituted ring couple to each other, while the two protons on the thio-substituted ring couple with themselves.

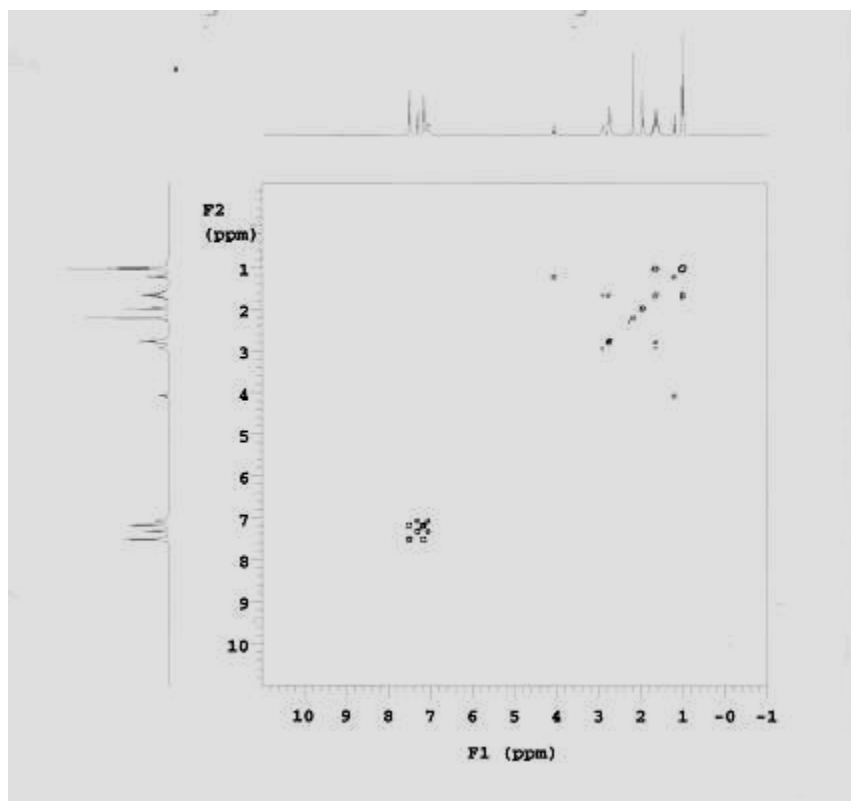


Figure 10 - COSY NMR of 4-monopropylthio-4',4''-dipropylsulfoxyltriphenylamine (**3**)

4,4',4''-tripropylsulfoxyltriphenylamine (**4**)

^1H NMR spectrum of **4** is shown below (Fig. 11) and is consistent with the spectra of **3** and **4**. Here, the peaks, previously identified as coming from the sulfoxyl-substituted ring now integrate to 6H each, while the thio-substituted peaks disappear. A chemical shift downfield is noted for the aromatic resonances of trisulfoxide species (**4**) with 7.54 and 7.24 ppm. The protons ortho to the sulfoxide fall approximately half way between the resonance of the thiol species (7.25 ppm) and the sulfone species (7.80 ppm).¹¹ Alkyl resonances appear as expected with the methylene bonded to the sulfoxide and the methyl being triplets, while the middle methylene is a multiplet.

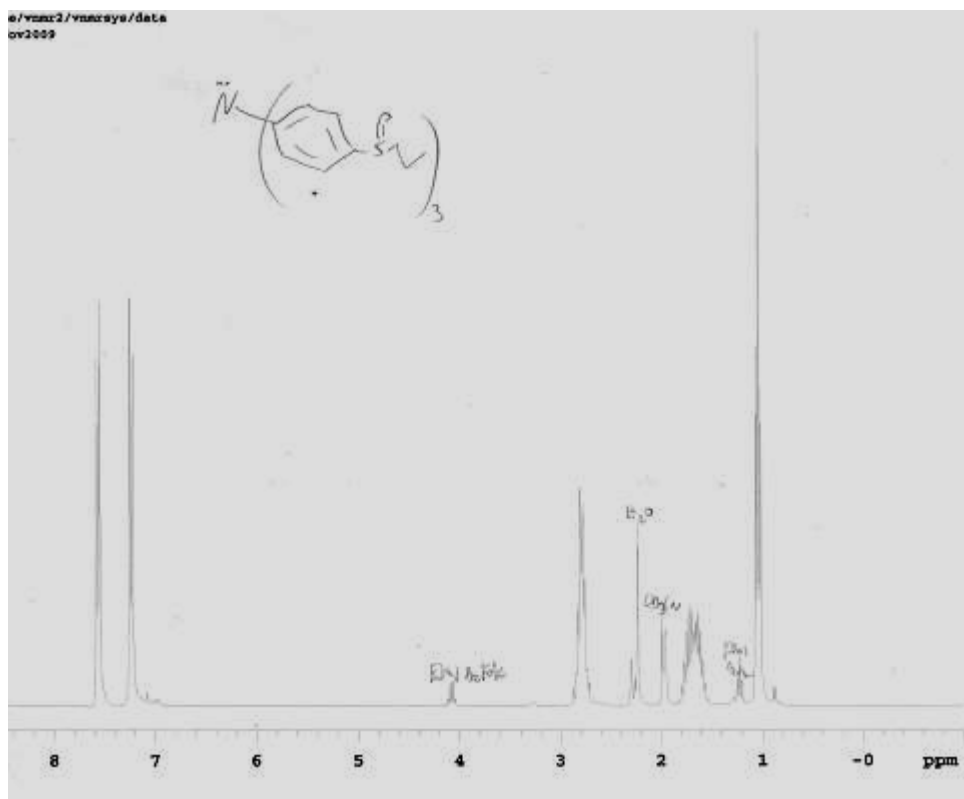


Figure 11 - ^1H NMR of 4,4',4''-tripropylsulfoxyltriphenylamine (**4**)

4,4',4''-tripropylsulfoxyltriphenylamine (**4**)

^{13}C NMR of **4** is shown below (Fig. 12) and further corroborates the characterization of this compound. Only three peaks are located in the alkyl region, as all of the propyl chains are bonded to the sulfoxide at all three positions. Four peaks appear in the aromatic region, as expected with all of the rings being equal and only four distinct carbons found in the *para*-substituted phenyl ring.

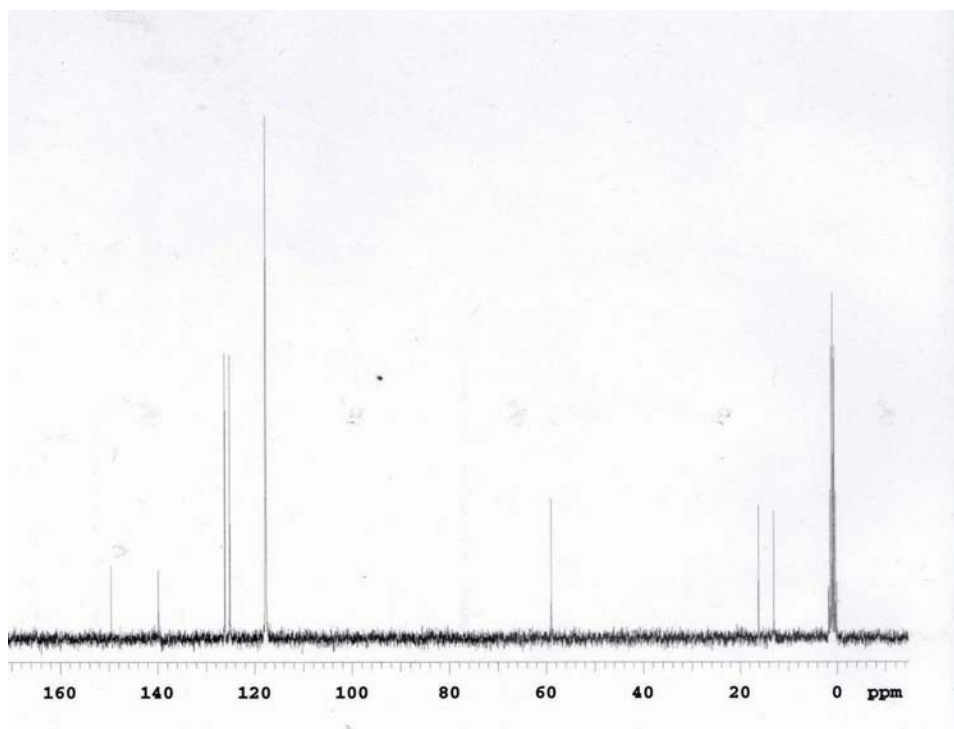


Figure 12 – ^{13}C NMR of 4,4',4''-tripropylsulfoxyltriphenylamine (**4**)

4,4',4''-tripropylsulfoxyltriphenylamine (**4**)

COSY NMR of **4** (Fig. 13) confirms the coupling between the aromatic protons and the coupling between the alkyl protons vicinal to each other, similarly as seen in **3** and **4**.

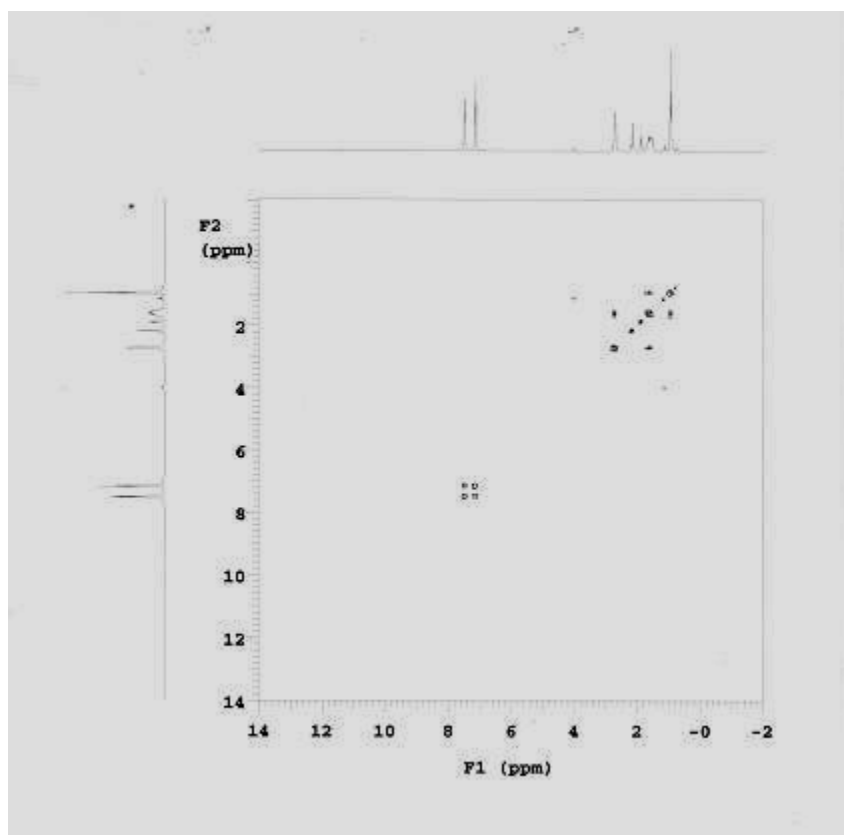


Figure 13 - COSY NMR of 4,4',4''-tripropylsulfoxyltriphenylamine (**4**)

4,4'-dipropylsulfoxyl-4''-monosulfonyltriphenylamine (**5**)

^1H NMR of **5** (Fig. 14) indicates four aromatic resonances. Two of those integrate to 4H each and show similar shifts to those seen in the trisulfoxide species (**4**) at 7.61 and 7.19 ppm. The other two resonances integrate to 2H each and show shifts more indicative of *tris*[4-propylsulfonyl]amine at 7.74 and 7.31 ppm.¹¹ In the alkyl region, the methylene group bonded to the sulfur is split into two resonances with the one shifted more downfield integrating in a ratio of 2H to 4H to the one shifted more upfield. The resonance integrating to 2H has a similar chemical shift to that of the *tris*[4-propylsulfonyl]amine at 3.13 ppm, indicating that it likely belongs to the sulfonyl-substituted ring instead of the sulfoxyl-substituted ring.

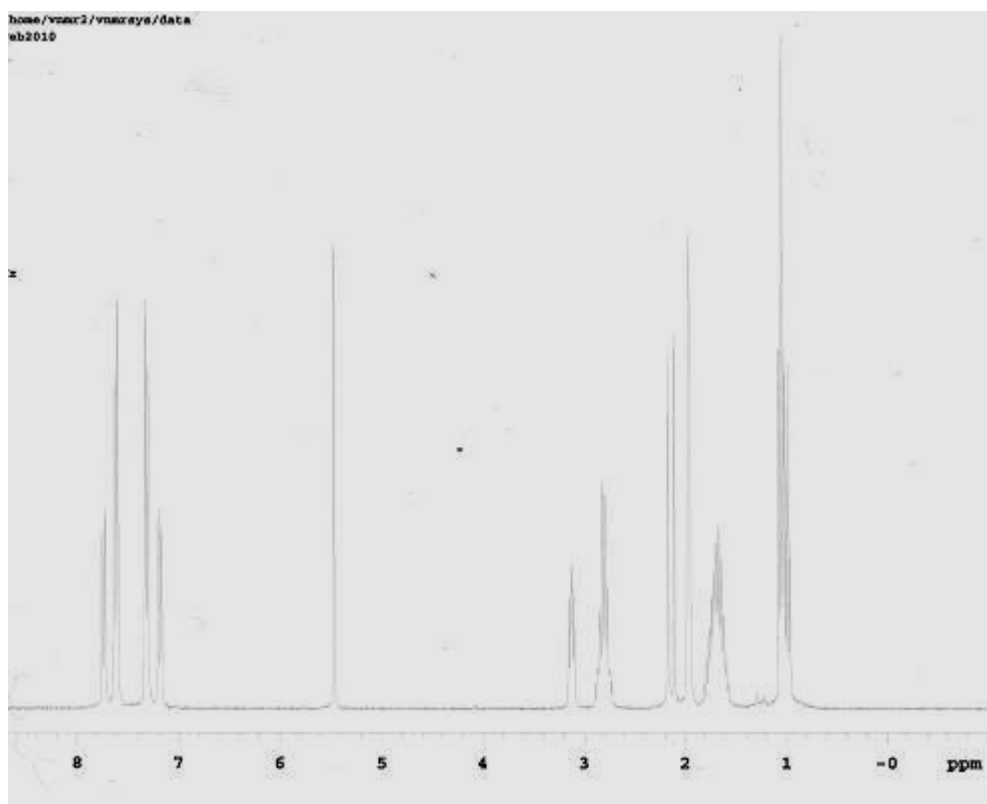


Figure 14 – ^1H NMR of 4,4'-dipropylsulfoxyl-4''-monosulfonyltriphenylamine (**5**)

4,4'-dipropylsulfoxyl-4''-monosulfonyltriphenylamine (**5**)

^{13}C NMR of **5** (Fig. 15) is similar to that of **2** in the alkyl region, as it indicates that there are two differently shifted propyl chains with 6 different carbons. The aromatic region shows 7 carbon peaks that indicate the presence of two differently substituted phenyl rings. The shifts observed for some peaks are also much more downfield, which is consistent with the fact that the sulfone group produces a more downfield shift than does the sulfoxide group.

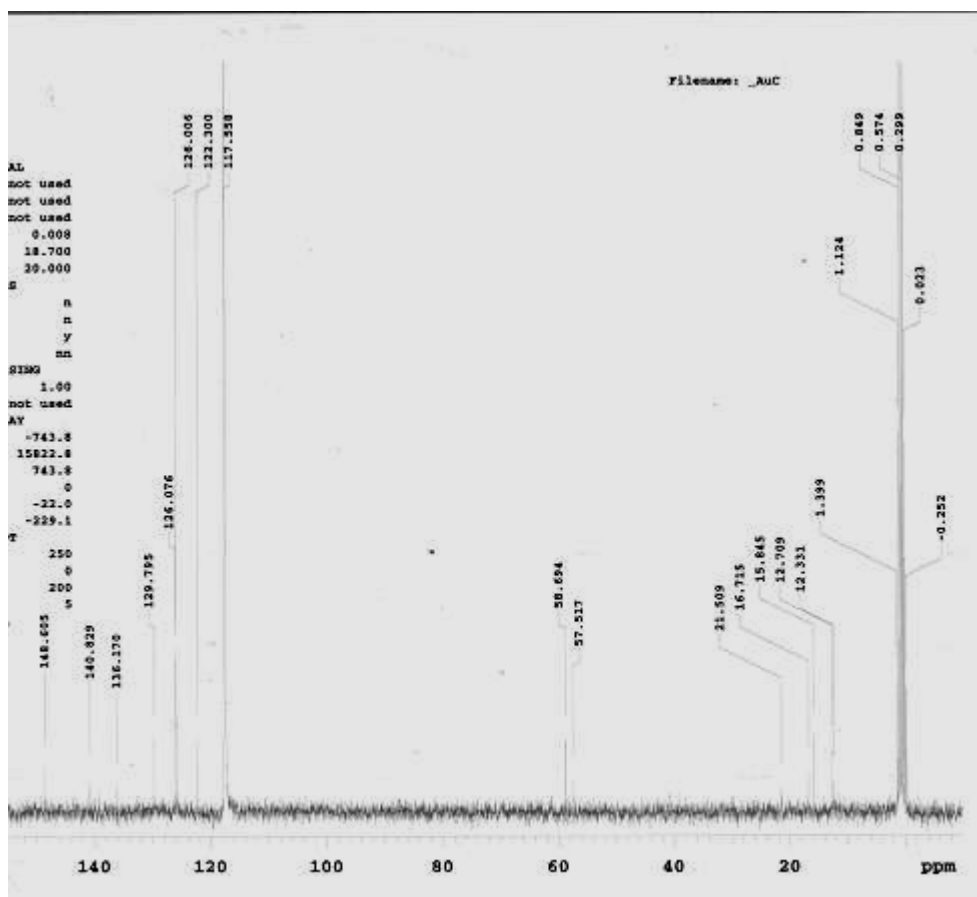


Figure 15 - ^{13}C NMR of 4,4'-dipropylsulfoxyl-4''-monosulfonyltriphenylamine (**5**)

4,4'-dipropylsulfoxyl-4''-monosulfonyltriphenylamine (**5**)

COSY NMR of **5** (Fig. 16) indicated the coupling of the alkyl protons to their vicinal neighbors, as observed in the previous spectra. The sulfonyl-substituted ring protons are coupled to each other in the aromatic region, while the sulfoxyl-substituted ring protons are coupled to themselves, as expected.

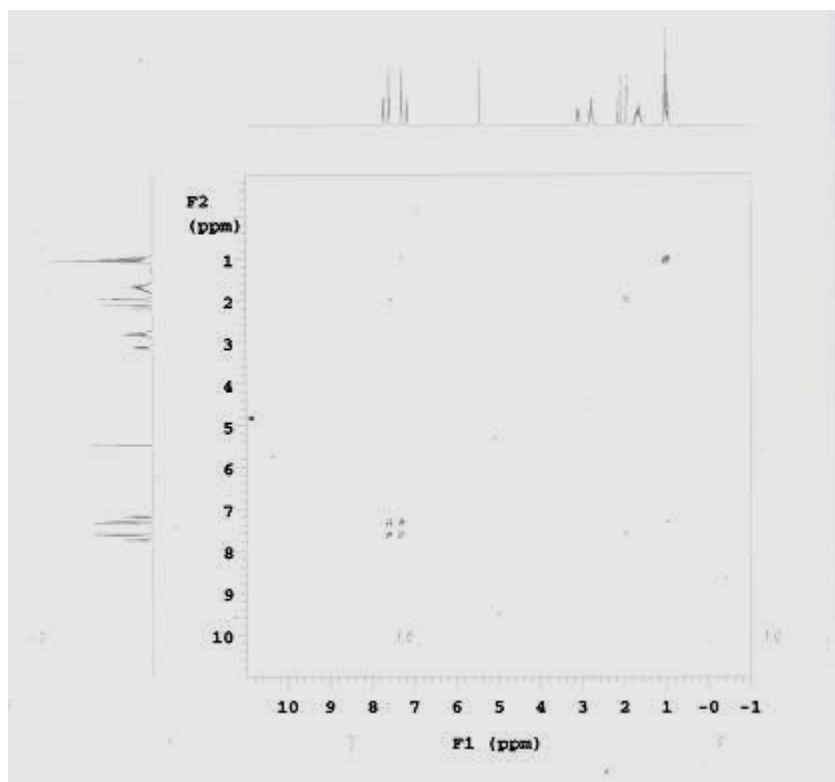


Figure 16 - COSY NMR of 4,4'-dipropylsulfoxyl-4''-monosulfonyltriphenylamine (**5**)

4,4'-dipropylsulfonyl-4''-monosulfoxyltriphenylamine (**6**)

^1H NMR spectrum of **6** shown below (Fig. 17) is similar to the spectrum obtained of **5**, except those resonances that were previously integrating in a 1:2 ratio, are now in a 2:1 ratio to each other. Hence, those resonances hypothesized to come from the sulfonyl-substituted ring are now twice the size of those peaks coming from the sulfoxyl-substituted ring consistent with the characterization of **6**. The methylene shifted most downfield is also now integrating in a 2:1 ratio with the sulfonyl-substituted ring in respect to the sulfoxyl-substituted ring.

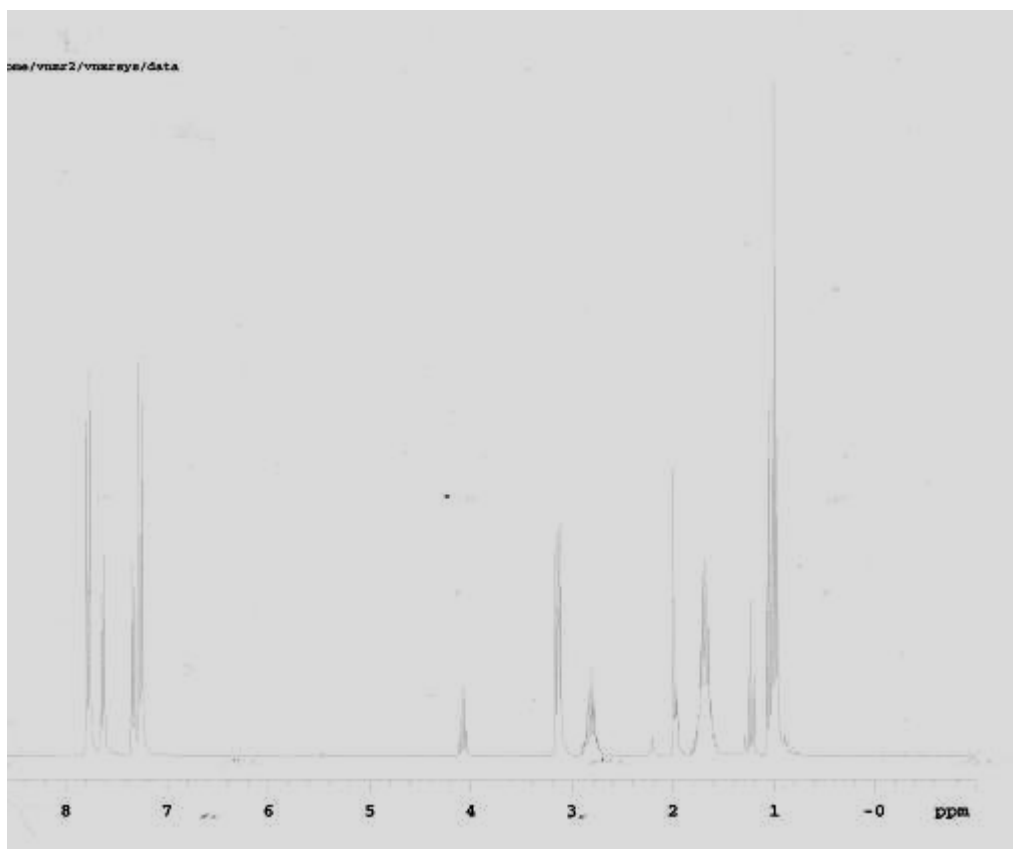


Figure 17 – ^1H NMR of 4,4'-dipropylsulfonyl-4''-monosulfoxyltriphenylamine (**6**)

4,4'-dipropylsulfonyl-4''-monosulfoxytriphenylamine (**6**)

^{13}C NMR of **6** shown below (Fig.18) shows the presence of two differently substituted rings with at least 8 carbon peaks in the aromatic region. Aside from the trace of ethyl acetate present in the spectrum, the alkyl region also indicates the presence of two differentially substituted rings.

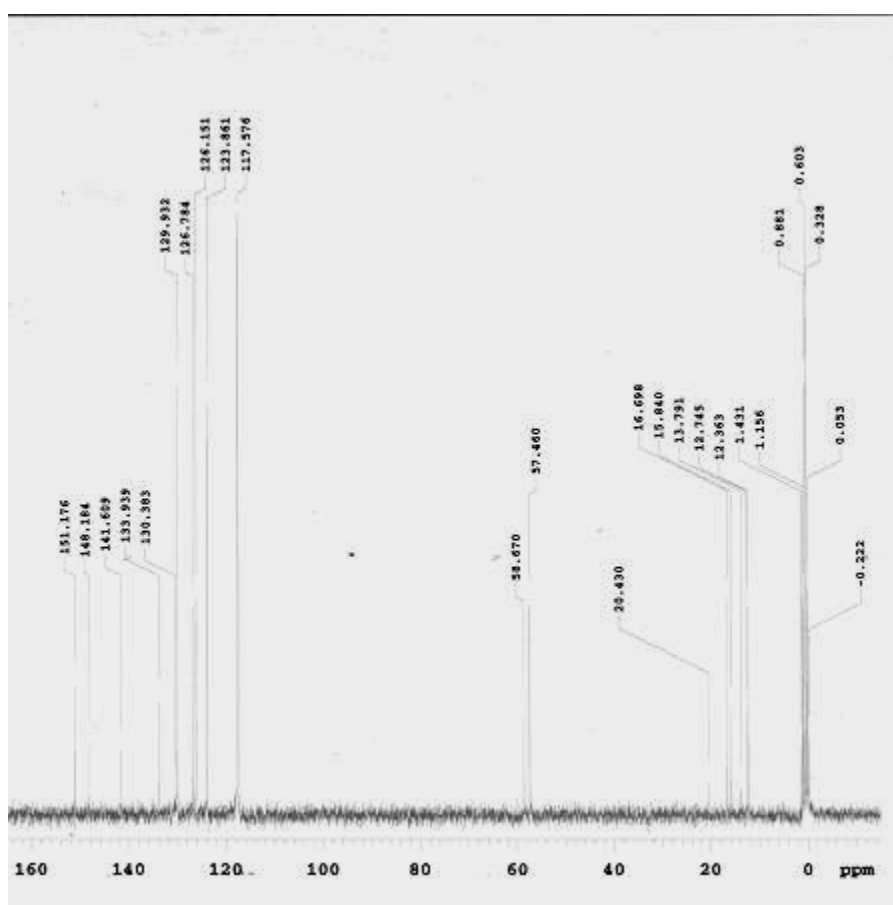


Figure 18 – ^{13}C NMR of 4,4'-dipropylsulfonyl-4''-monosulfoxytriphenylamine (**6**)

4,4'-dipropylsulfonyl-4''-monosulfoxyltriphenylamine (**6**)

COSY NMR spectrum of **6** (Fig. 19) is shown below and shows coupling between the aromatic protons and the alkyl protons through the sulfur. Once again the aromatic resonances on the sulfoxyl ring correspond to each other, while the sulfonyl resonances correspond more closely with themselves. The alkyl chain also shows that those protons that are vicinal neighbors are coupled to each other.

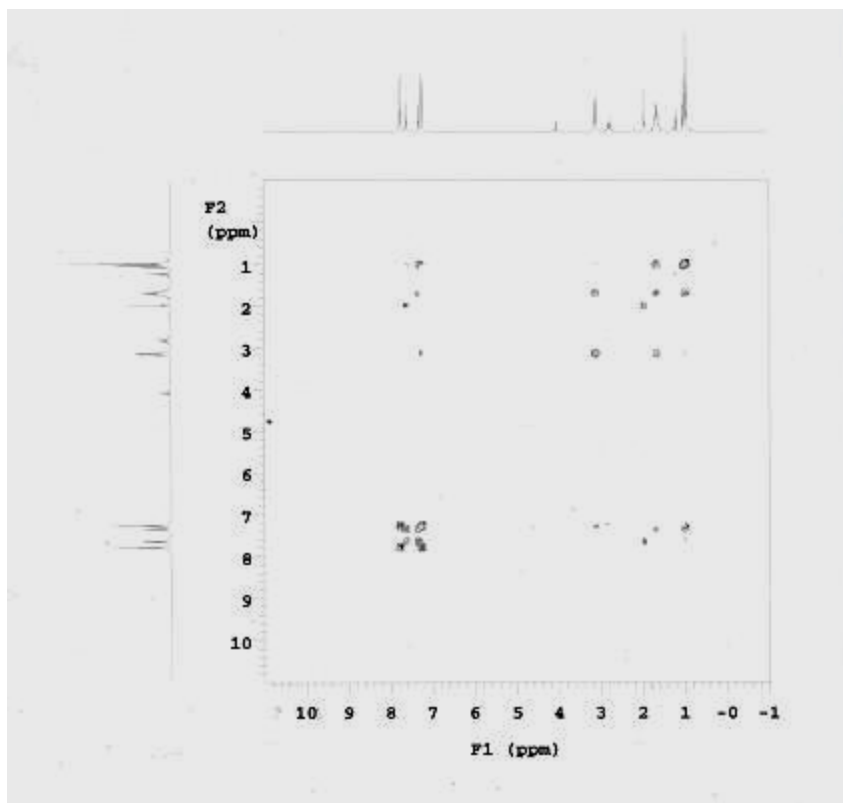


Figure 19 - COSY NMR of 4,4'-dipropylsulfonyl-4''-monosulfoxyltriphenylamine (**6**)

RESULTS

Resolving the number of stereoisomers in the ^{13}C NMR and ^1H NMR spectra proved to be unsuccessful, as could be seen through the spectra shown in the previous section for each compound. The only carbon peaks observed were the ones that were expected. All of the carbon spectra were obtained on a 300MHz NMR with CD_3CN as the solvent.

Attention was then turned to chiral shift reagents. The first used was $\text{Eu}(\text{tfc})$ utilizing CD_3CN as the solvent. The shift reagent was first dried over 48 hours *in vacuo* over P_2O_5 . A small amount of the reagent (~3 mg) was placed in the NMR tube, making sure that the molar amount of the shift reagent placed in there was much smaller than the molar amount of the substrate (approximately 1:5 in this case). A ^1H NMR spectrum (Fig. 20) was then obtained.

The spectrum, however, has not been obtained consistently and has not been reproduced, despite multiple attempts to recreate the conditions under which this one was obtained. Despite varying the concentration of the shift reagent, no stereochemical discrimination was noted in other spectra. Benzene- D_6 was also used once, but failed to shift the different stereoisomers.

The spectrum below (Fig. 20) shows that there are in fact a number of diastereomers present in the solution of Eu(tfc) with 4,4',4''-tripropylsulfoxyltriphenylamine (**4**). There are pronounced shifts for a number of diastereomers for all resonances. Further analysis of the spectrum is presented in the next section.

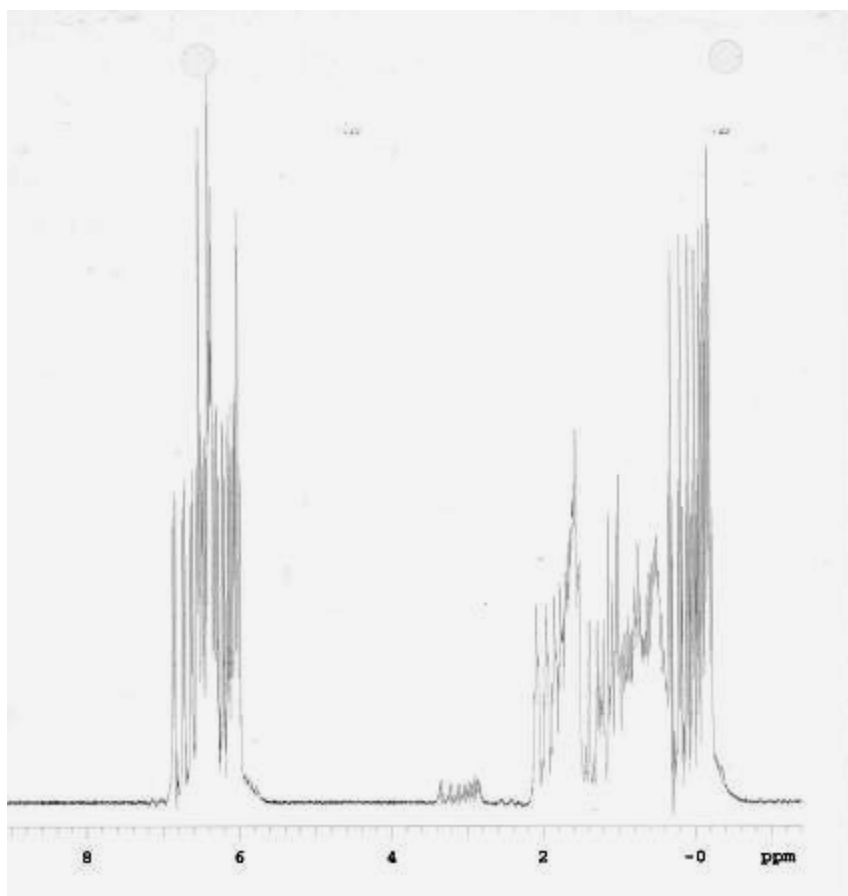


Figure 20 – ^1H NMR spectrum of 4,4',4''-tripropylsulfoxyltriphenylamine (**4**) with Eu(tfc).

DISCUSSION

For 4,4',4''-tripropylsulfoxyltriphenylamine (**4**), there should be 6 different resonances observed in a ^1H NMR if the exchange between the chiral shift reagent and the sulfoxide is fast. Slow exchange would indicate an extra resonance corresponding to the non-complexed sulfoxide and appear similar to one that is observed in a spectrum taken without a shift reagent present in the sample. The resonance would still be observed at a different chemical shift. Given that there are three stereocenters in each molecule and that there two possible stereoisomers possible at each one (R and S), then the following would represent the possible complexes formed by the Eu(tfc) and **4**:

RRR[R], SSS[R], SSR[R], [R]SSR, SRR[R], [R]SRR. The stereoisomer in brackets represents the shift reagent and was chosen arbitrarily to be R here, for illustrative purposes. Note that the shift reagent, represented by [R], can complex with either the R or the S center in each stereoisomer.

For **2**, there should be only two possible complexes given fast exchange, since there is only one sulfoxide present. The possible resonances observed would arise from R[R] and S[R]. For **3**, the number of possible resonances would be four with fast exchange given that RR[R], SS[R], RS[R], [R]RS would be formed.

In an e-mail correspondence, Thomas J. Wenzel stated that usually sulfoxides are known to have fast exchange with lanthanide shift reagents.¹⁸ The presence of the unbound form can usually be identified, as the bound form results in significant line broadening. This suggests that the spectrum observed here (Fig. 20) indicates fast exchange, as the resonances appear to exhibit a similar level of line broadening,

supporting the claim that sulfoxides do experience fast exchange with lanthanides. Temperature has been reported as one of the conditions that affects the rate of the exchange,⁹ but the temperature would have to be lowered significantly in order to noticeably lower its speed.¹⁸

Below is the ¹H NMR spectrum (Fig. 21) showing the different diastereomers of the sulfur center with respect to the resonance of the methylene bonded directly to the sulfur. The resonances appear to all be quartets, where they would be expected to be observed as triplets. The integration of these resonances indicates that there are approximately 6.7 resonances. Visually there appears to be 7-8 different quartets present. The coupling to an extra proton likely arises from the presence of an extra proton from the Eu complex.

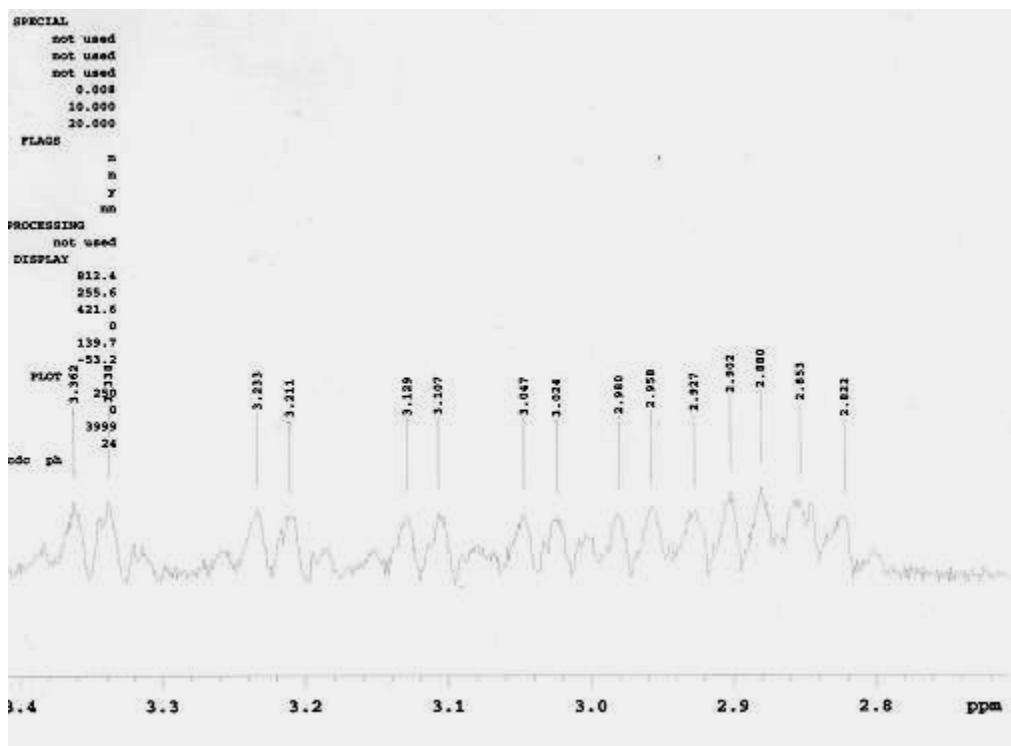


Figure 21 - The expanded 2.7 – 3.4 ppm region of ¹H NMR spectrum of 4,4',4''-tripropylsulfoxyltriphenylamine (**4**) with Eu(tfc).

Below is the ^1H NMR spectrum (Fig. 22) showing the different diastereomers of the 2.2 - -0.3 ppm region of the spectrum. Although most of these peaks display the presence of a number of different diastereomers, only the resonances corresponding to the methyl can be analyzed with a level of accuracy (0.3 - -0.2). The integration of that part of the spectrum suggested that there are 7.1 resonances, although visually between 7 and 8 can be observed.

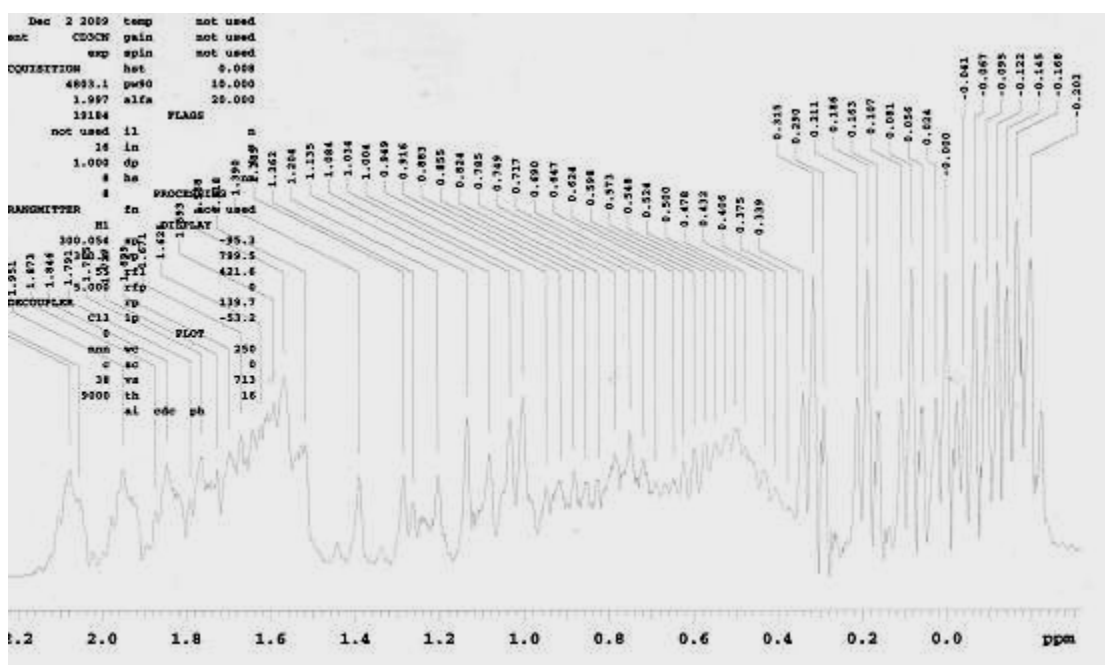


Figure 22 - The expanded 2.2 – -0.3 ppm region of ^1H NMR spectrum of 4,4',4''-tripropylsulfoxyltriphenylamine (**4**) with Eu(tfc).

Below is the ^1H NMR spectrum (Fig. 23) showing the different diastereomers in the aromatic region. There are two different types of protons in the compound, so the number of resonances observed in the spectrum correspond to two, rather than just one proton. Integration suggested that there are approximately 16.44 resonances between the two protons, averaging 8.22 per proton. Visual estimation shows that there are 14-16 resonances present in the spectrum, which indicates that there are between 7 and 8 diastereomers formed per each proton.

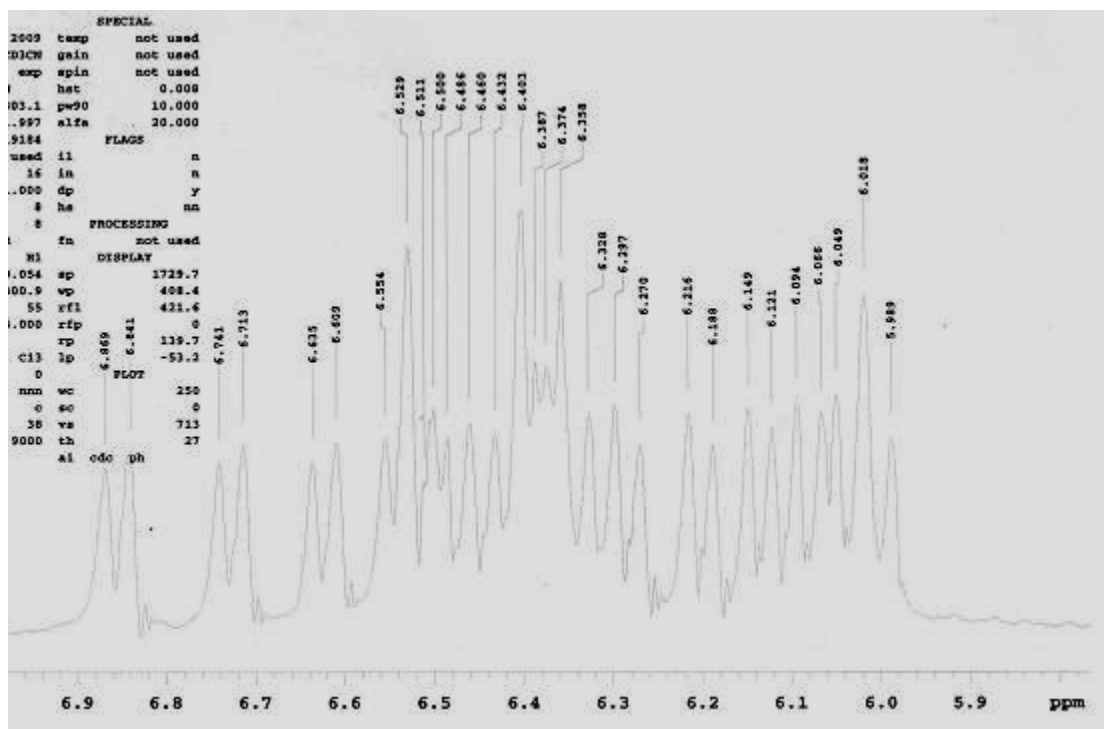


Figure 23 - The expanded 6.9 – 5.9 ppm region of ^1H NMR spectrum of 4,4',4''-tripropylsulfoxyltriphenylamine (**4**) with Eu(tfc).

The data does not show consistently exactly how many stereoisomers are present in **4**. Although six different stereoisomers are expected, the data collected suggests that either 7 or 8 are present. The extra resonances may arise from the complexing of multiple Eu(tfc) molecules to one triphenylamine molecule. The presence of Eu(tfc) certainly affects the electronics of the substrate molecule with the electron-withdrawing effect of the fluorine containing shift reagent likely producing a more electro-positive lanthanide ion.⁴

Steric effects in the complexing event are also important to consider.⁹ The phenyl group on one side of the sulfoxide, along with a propyl group on the other side likely may result in a considerable amount of steric hindrance in the complexing.

The relatively equal size of each resonance of each diastereomer formed in the spectrum obtained here (Fig. 20) indicates that there are equal amounts of each diastereomer. A major assumption of the experiment is that *m*-CPBA oxidizes the thiol resulting in a racemic mixture. If the reaction would favor the formation of the R or the S conformation, then it would be much more difficult to identify the number of stereoisomers present in the compound. The assumption that *m*-CPBA does produce a racemic mixture is reasonable given the lack of a chiral center in the molecule.

Another major consideration of discriminating between different chiral compounds through NMR spectroscopy is the choice of solvent. Using CD₃CN as the solvent was initially considered advantageous during the identification of each of the sulfur-containing triphenylamines due to the fact that its solvent peak is not observed in the aromatic region. This solvent also did not overlap with any of the alkyl peaks in the original spectrum (Fig. 11). Acetonitrile, however, is quite polar and is likely to

competitively solvate the europium ion. The nucleophilic character of acetonitrile would also contribute to its ability in solvating the shift reagent. Hence, the use of a more non-polar solvent, such as benzene, may be more advantageous to this study.

Previous literature indicates that the optimal conditions to resolve the different stereoisomers are difficult to predict.⁴ In the study of paramagnetic shift reagents reported by Wenzel et. al.,⁴ no consistency was observed whether either trifluoro camphorate (tfc) or heptafluoro camphorate (hfc) should be used for a particular compound. While the complexation with hfc may be stronger due to the resulting more positive lanthanide ion, tfc in many cases is a more optimal reagent for discrimination of different stereoisomers. The extent of the observed line broadening as a result of the use of lanthanide reagents is proportional to the square of the chemical shift induced, so those reagents that cause more shift will also result in more line broadening and less clear data.¹⁹

Given the complexity of the system studied here, the conditions for resolving the different stereoisomers will have to be optimized for a number of conditions. One approach could involve obtaining spectra with the gradual addition of very small amounts of a well-dried shift reagent (<1mg). This would likely elucidate the appropriate concentration of reagent necessary, as well as show the gradual shift of each stereoisomer. This would in turn help distinguish the number of stereoisomers present more clearly. Extra care should be taken to completely dry the reagents, as they pick up moisture quickly rendering them less effective. The use of a higher-field NMR would also likely result in more informative spectra. Trials at different solvents and using different reagents should also be completed, as they may prove more

effective in the discrimination of the stereoisomers. Other reagents utilize samarium(III),²⁰ cerium(III),²⁰ and lanthanum(III).²¹

Lastly, it should be noted that the spectrum obtained in this experiment does indeed show the presence of different stereoisomers in the 4,4',4''-tripropylsulfoxyltriphenylamine (**4**) and indicates that the desired discrimination in chirality can be feasibly studied further with success, although the optimal conditions for such discrimination may be very specific and difficult to determine.

EXPERIMENTAL

^1H , COSY, and ^{13}C NMR spectra were measured using Varian Mercury Vx 300MHz pulsed field gradient spectrophotometer. High Resolution Mass Spectroscopy was performed by the University of California – Riverside High Mass Spectroscopy Facility.

4,4'-dipropylthio-4''-monopropylsulfoxyltriphenylamine (2) and 4-monopropylthio-4',4''-dipropylsulfoxyltriphenylamine (3) and 4,4',4''-tripropylsulfoxyltriphenylamine (4). At 0°C , *m*-chloroperoxybenzoic acid (85mg, 0.64mmol) was added to a solution of 4,4',4''-tripropylthiotriphenylamine (**1**) (100mg, 0.21mmol) in 25mL of CH_2Cl_2 . The reaction was stirred vigorously for 6 hours in a 50mL roundbottom flask on ice. Approximately 25mL of NaHCO_3 was added to the reaction mixture and stirred for 10 minutes. The organic layer was then washed with H_2O (3 x 30mL) and then dried with Na_2SO_4 . The solvent was removed by rotary evaporation. The mixture was purified by flash chromatography using silica with 1:9 methanol / ethyl acetate.

4,4'-dipropylthio-4''-monopropylsulfoxyltriphenylamine (2). White solid. M.P. = $45 - 47^\circ\text{C}$. ^1H NMR (300MHz, CD_3CN): $\delta = 7.46$ (d, $J = 8.1\text{Hz}$, 2H), 7.29 (d, $J = 6.9\text{Hz}$, 4H), 7.07 (d, $J = 8.7\text{Hz}$, 2H), 7.03 (d, $J = 6.9\text{Hz}$, 4H), 2.91 (t, $J = 7.5\text{Hz}$, 4H), 2.75 (t, $J = 7.5$, 2H), 1.65 (m, $J = 7.5\text{Hz}$, 6H), 1.02 (t, $J = 7.8\text{Hz}$, 9H). ^{13}C NMR (300MHz, CD_3CN): $\delta = 150.2, 144.9, 136.8, 132.4, 130.4, 125.9, 125.6, 122.0, 58.8, 35.5, 22.5, 15.9, 12.8, 12.7$

4-monopropylsulfoxyl-4',4''-dipropylsulfoxyltriphenylamine (3). White oil. ^1H NMR (300MHz, CD_3CN): $\delta = 7.52$ (d, $J=8.4\text{Hz}$, 4H), 7.33 (d, $J=8.7\text{Hz}$, 2H), 7.18 (d, $J=8.4\text{Hz}$, 4H), 7.07 (d, $J=8.1\text{Hz}$, 2H), 2.93 (t, $J=7.5\text{Hz}$, 2H), 2.77 (m, $J=7.2$, 4H), 1.66 (m, $J=7.5\text{Hz}$, 6H), 1.03 (t, $J=7.5\text{Hz}$, 9H). ^{13}C NMR (300MHz, CD_3CN): $\delta = 149.9$, 138.7, 130.5, 126.9, 126.0, 124.0, 59.0, 35.5, 22.7, 16.2, 12.9

4,4',4''-tripropylsulfoxyltriphenylamine (4)

White solid. M.P. = 101 – 103°C. White solid. ^1H NMR (300MHz, CD_3CN): $\delta = 7.57$ (d, $J=8.1\text{Hz}$, 6H), 7.24 (d, $J=8.4\text{Hz}$, 6H), 2.79 (m, $J= 8.4\text{Hz}$, 6H), 1.66 (m, $J=6.9\text{Hz}$, 6H), 1.04 (t, $J=7.5\text{Hz}$, 9H). ^{13}C NMR (300MHz, CD_3CN): $\delta = 149.5$, 139.8, 126.1, 125.1, 58.9, 16.1, 12.9

4-monopropylsulfonyl-4'',4'-dipropylsulfoxyltriphenylamine (5) and 4,4'-

dipropylsulfonyl-4''-monopropylsulfoxyltriphenylamine (6). Clear oil. At 0°C, *m*-chloroperoxybenzoic acid (409mg, 2.3mmol) was added to a solution of 4,4',4''-tripropylthiotriphenylamine (172mg, 0.4mmol) in 50mL of CH_2Cl_2 . The reaction was stirred vigorously for 6 hours in a 100mL roundbottom flask on ice. Approximately 25mL of NaHCO_3 was added to the reaction mixture and stirred for 10 minutes. The organic layer was then washed with H_2O (3 x 30mL) and then dried with Na_2SO_4 . The solvent was removed by rotary evaporation. The mixture was purified by flash chromatography using silica with 1:9 methanol / ethyl acetate.

4-monopropylsulfonyl-4'',4'-dipropylsulfoxyltriphenylamine (5). White solid.

M.P. = 131 – 134°C. ^1H NMR (300MHz, CD_3CN): $\delta = 7.74$ (d, $J= 8.4\text{Hz}$, 2H), 7.61 (d, $J=8.1\text{Hz}$, 4H), 7.31 (d, $J=7.5\text{Hz}$, 4H), 7.19 (d, $J=8.1\text{Hz}$, 2H), 3.13 (t, $J= 8.4\text{Hz}$,

2H), 2.80 (m, J=7.8Hz, 4H), 1.68 (m, J=7.2Hz, 6H), 1.05 (m, J=7.5Hz, 9H). ¹³C NMR (300MHz, CD₃CN): δ = 148.6, 140.8, 136.2, 129.8, 126.1, 126.0, 122.3, 58.7, 57.5, 21.5, 16.7, 15.8, 12.7, 12.3

4,4'-dipropylsulfonyl-4''-monopropylsulfoxyltriphenylamine (6). White solid.

M.P = 129-132°C. ¹H NMR (300MHz, CD₃CN): δ = 7.78 (d, J=8.7Hz, 4H), 7.64 (d, J=9.0Hz, 2H), 7.33 (d, J=8.4Hz, 2H), 7.26 (d, J=9.0, 4H), 3.14 (t, J= 8.1Hz, 4H), 2.81 (m, J=7.2Hz, 2H), 1.68 (m, J= 8.1Hz, 6H), 1.01 (m, J=7.5Hz, 9H). ¹³C NMR (300MHz, CD₃CN): δ = 151.2, 148.2, 141.6, 133.9, 130.4, 129.9, 126.8, 126.2, 123.9, 57.5, 16.7, 15.8, 12.8, 12.4

Chiral Shift Reagent

Eu(tfc) was first dried *in vacuo* over P₄O₁₀ at around 80°C for approximately 48 hours. A milligram of material or less was slowly added to a standard NMR tube containing the triphenylamine substrate in CD₃CN and a ¹H NMR spectrum was obtained. Spectra were then obtained with the addition of increasing amounts of Eu(tfc). Benzene-D₆ was also used as an NMR solvent at one point, but no spectrum is reported here as it did not prove effective in stereochemical discrimination. The sample was at room temperature when all NMR spectra were obtained.

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**II. Synthesis of Triphenylamine Electrocatalysts:
Nitration of *tris*[4-propylsulfonylphenyl]amine**

INTRODUCTION

Triphenylamines are tertiary amines and can be considered derivatives of ammonia where the three hydrogen atoms are replaced with aryl groups.

Triphenylamines and their derivatives have a large number of industrial applications primarily due to the formation of a stable aminium radical cation.¹ The radical cation arises with the removal of an electron from the central nitrogen's pair. Arylamines are used in conductive polymers,² pharmaceuticals,³ electro photography,⁴ electrochemistry,⁵ biosensors⁶ among others. These compounds are weakly basic and rarely form salts. They are also considered carcinogenic and long-term exposure has been linked to liver and kidney damage in animal studies.¹

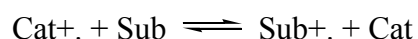
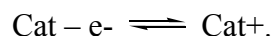
The intended application of the triphenylamines described here is for their use as electrocatalysts. Steckhan and co-workers showed that brominated triphenylamines can be used as electrocatalysts to oxidize a large variety of organic compounds.⁷ Fry has reported anodic electrocatalytic oxidation of electronegatively substituted alkenes bearing electron-withdrawing groups. Brominated triphenylamines, however, are not useful electrocatalysts for these reactions.⁵ Triphenylamine electrocatalysts (Fig. 1) with higher oxidation potentials are needed, as to minimize the difference between the oxidation potential of the catalyst and that of the substrate, thus increasing the efficiency of the catalyst. Computational methods have been applied to predict possible triphenylamine electrocatalysts that would be successful catalysts.⁵ Through the addition of different electron-withdrawing groups to the aryl rings of the triphenylamines, a catalyst with a higher oxidation potential can be obtained, as has

been done with the addition of sulfone groups, nitro groups, and chlorine groups.⁵

Previously, the direct anodic oxidation of stilbenes bearing strong electron-withdrawing groups in methanol was reported. In this situation, the oxidation potential of the stilbenes is close to that of the solvent.^{8,9} In order to consume the starting material to yield the oxidized product, a significant excess of current had to be passed through the solution. This is not only inefficient, but it also leads to a number of undesired side products in the reaction as the solvent itself is oxidized. The use of metal catalysts to perform the oxidations is also undesirable as these metals are known to be toxic, expensive, and cannot be used to perform these reactions in an undivided cell.¹⁰

Indirect oxidation through mediated electron transfer was proposed as a possible technique in improving the anodic oxidation of these stilbenes.¹⁰ Here, an electron-transfer catalyst with a lower oxidation potential than the substrate is employed where the oxidation of the catalyst results in a stable cation radical intermediate. This cation catalyst can then in turn abstract an electron from the substrate, leading a cascade reaction where this thermodynamically unfavorable abstraction step is followed by a fast reaction of the substrate radical to products. This reaction can be successfully carried out with the substrate's oxidation potential being almost 0.5V higher than that of the catalyst. Triphenylamines were suggested as potential catalysts due the stability of the radical cation at the central nitrogen, along with the ability to control the oxidation potential of these compounds by the addition of different functional groups onto the aryl rings. The oxidations are performed in an undivided cell using a platinum cathode, carbon anode, and a coulometer at a

potential around the potential of the catalyst measured against Ag/AgNO₃ in 10-20mL of electrolyte solution containing acetonitrile with a small amount of water (<1mL). A fraction of the cation radicals of the catalyst are converted back to the neutral amine, requiring additional current. The diagram below shows the general mechanism by which these anodic oxidations occur.¹⁰



Schmidt and Steckhan found that the oxidation potential of the triphenylamine catalysts increase with a greater number of bromine atoms in the compound.⁷ Since the electron-withdrawing property of the nitro group (-NO₂) is much greater than that of bromine, the attention of the Fry group turned to the synthesis of nitrated triphenylamines. Unfortunately, the 4,4',4''-nitrotriphenylamine (**1**) was found to have poor solubility in the desired solvents.¹¹ Hence, 4,4',4''-methyl-2,2',2''-nitrotriphenylamine (**2**) has been of much interest to the Fry group as it provides a relatively higher oxidation potential at 1.28V, along with good stability and solubility.¹⁰

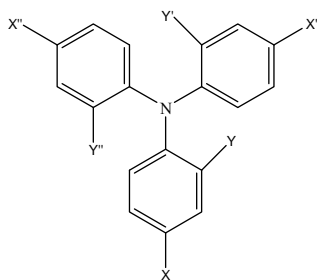


Figure 1 –Triphenylamine electrocatalysts

1. $X=X'=X''=NO_2$; 4,4',4''-nitrotriphenylamine
2. $X=X'=X''=CH_3$; $Y=Y'=Y''=NO_2$; 4,4',4''-methyl-2,2',2''-nitrotriphenylamine
3. $X=X'=X''=Cl$; $Y=Y'=Y''=NO_2$; 4,4',4''-trichloro-2,2',2''-trinitrotriphenylamine
4. $X=X'=X''=SCH_2CH_2CH_3$; 4,4',4''-tripropylthiotriphenylamine
5. $X=X'=X''=SO_2CH_2CH_2CH_3$; 4,4',4''-tripropylsulfonyltriphenylamine

Since the addition of a nitro group on a benzene ring deactivates the ring significantly, nitration is usually best performed as the last step of a multi-step synthesis. In the synthesis of 4,4',4''-methyl-2,2',2''-nitrotriphenylamine (**2**), the nitration is performed on 4,4',4''-tritolyamine.¹¹ Vigorous conditions are often used in order to polynitrate a single benzene ring due to this effect. Triphenylamines are more readily nitrated due to the activating effect of the central nitrogen.

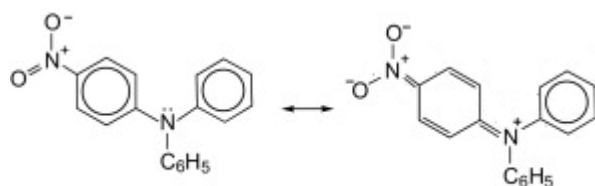


Figure 2 – Resonance structures of a para-nitrated triphenylamine.⁵

The presence of a nitro group at the para position of the rings has a significant effect on the geometry of the overall compound.⁵ The quinoid structure, shown in the figure above (Fig. 2), is believed to be a strong contributor to the overall resonance

hybrid of the molecule. Calculations suggest major bond length alterations with the presence of the nitro group at the para position, little alternations at the meta position, and some level of alternation at the ortho position. With the formation of the radical cation, the geometry changes as an electron is removed from the lone pair. The quinoid resonance structure would likely include the donation of an electron from one of the oxygen atoms of the nitro group.⁵

Recently, the 4,4',4''-trichloro-2,2',2''-trinitrotriphenylamine (**3**) has been synthesized,⁵ but proved to be unstable with the chlorine groups in the para position and ineffective as a catalyst despite a high oxidation potential of 1.56V.

Oxidation of 4,4',4''-tripropylthiotriphenylamine (**4**) results in 4,4',4''-tripropylsulfonyltriphenylamine (**5**), which has a potential of 1.15V.⁵ In the present work, it has been proposed to synthesize a nitrated 4,4',4''-tripropylsulfonyltriphenylamine (**5**) as a potentially effective and stable electrocatalyst. The 4,4',4''-tripropylsulfonyltriphenylamine (**5**) catalyst is readily soluble in a number of solvents.⁵ The addition of one or even two nitro groups is expected to significantly raise the oxidation potential of the catalyst and make it more effective in reactions involving alkenes bearing strong electron-withdrawing groups.

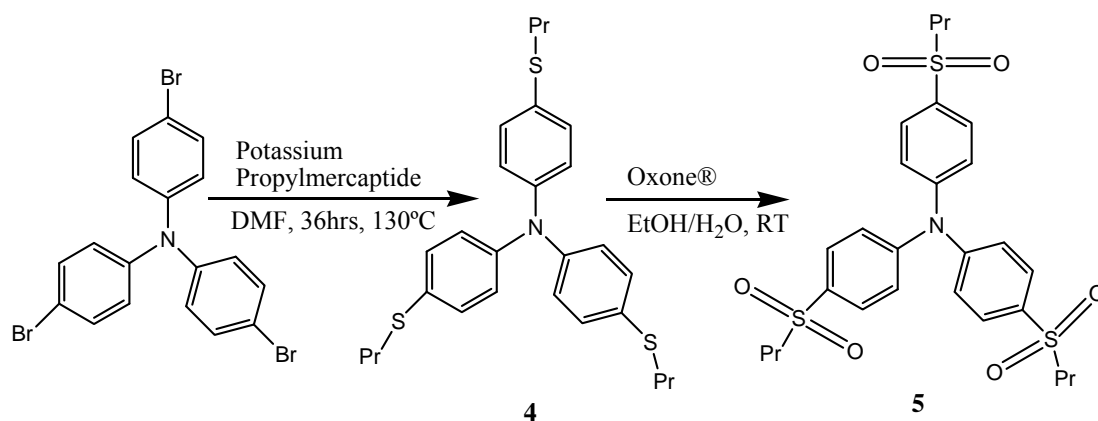


Figure 3 – The synthesis of 4,4',4''-tripropylsulfonyltriphenylamine (**5**) as reported by Wu, X. et. al.⁵

Desired Products:

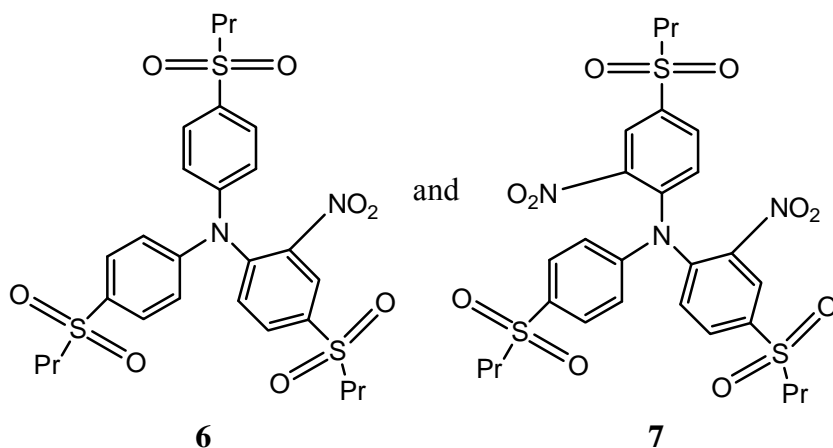


Figure 4 – The desired products of the nitration of 4,4',4''-tripropylsulfonyltriphenylamine (**5**).

SYNTHESIS

A. Preparation of *tris*[4-propylsulfonylphenyl]amine (**5**)

The preparation of *tris*[4-propylthiolphenyl]amine (**4**) was performed as described⁵ starting with *tris*[4-bromophenyl]amine. Approximately 7 equivalents of potassium mercaptide was added to 4,4',4''-tribromotriphenylamine in DMF over 43 hours at 130°C. The reaction was significantly scaled up from the previously described procedure since more product was necessary. Less solvent was used and the reaction was run longer at a slightly higher temperature. These differences resulted in an increase in yield from 35% to 60%. The extracted crude product required purification using flash chromatography as there were a number of impurities, including products where the substitution occurred at only one or two of the phenyl rings instead of three. It should be noted that this compound does not crystallize readily and has to be very pure in order to do so. The oxidation of **4** with OXONE® (potassium peroxymonosulfate) was performed exactly as described in literature⁵ and resulted in the synthesis of **5** with the same yield of 81% as described earlier.

An alternate synthesis of **5** was developed based on the use of *m*-chloroperoxybenzoic acid (*m*-CPBA) in oxidations of sulfides to sulfones.¹² This reaction involved placing **4** in dichloromethane with *m*-CPBA and stirring the solution vigorously for 6 hours on ice. This reaction produced **5** in a 78% yield after it was purified through recrystallization in 95% EtOH.

B. Nitration of *tris*[4-propylsulfonylphenyl]amine

The solubility of the nitrated 4,4',4''-tripropylsulfonyltriphenylamine (**5**) will have to be closely noted as the addition of polar functional groups may result in the overall compound being too polar and insoluble in some organic solvents. As these compounds had never been synthesized and isolated, an appropriate method of aromatic nitration needed to be identified. The nitration of 4,4',4''-trichlorotriphenylamine to yield 4,4',4''-trichloro-2,2',2''-trinitrotriphenylamine (**3**) was successfully carried out using sodium nitrate in trifluoroacetic acid.⁵ These reaction conditions appeared to be promising in potentially nitrating the sulfonyl species.

Compound **5** was nitrated using NaNO₂ in trifluoroacetic acid (TFA).⁵ It has been found that controlling the stoichiometric amount of NaNO₂ results in the major product being either the mono-nitro derivative (**6**) or the di-nitro derivative (**7**). With the addition of the nitrating reagent, a rubber septum should be placed to close the flask, as some of the nitrogen-containing gases (i.e. N₂O₄, NO) escape, lowering the yield. For the highest yield of **6**, a 1:1 ratio of NaNO₂ to starting material is used and the reaction is run for one hour at 0 - 5°C, as it slows down the formation of **7**. If the major product desired is **7**, then the reaction can be run at room temperature for one hour and a 3:1 ratio of NaNO₂ to starting material is appropriate. Due to the slight solubility of **6** and **7** in water, cold water was used in order to maximize the yield in the reaction. The reaction results in a mixture of the mono-nitrated and the di-nitrated

product. The mixture is easily purified by flash chromatography. Unlike compound **5**, compounds **6** and **7** do not crystallize easily and an extra recrystallization step is needed to obtain crystals of the compound. ^1H NMR, COSY NMR, ^{13}C NMR spectroscopy and elemental analysis were utilized to confirm the identity of these compounds.

The ^1H NMR spectrum of 4,4',4''-tripropanesulfonyl-2-nitrotriphenylamine (**6**), Figure 5 on the next page, corresponds to the assigned structure. As expected five resonances appear in the aromatic region, two belonging to the non-nitrated ring and both integrate to 4H. The remaining three proton resonances belong to the nitrated ring with the most downfield resonance appearing as a singlet integrating to one proton. Four of resonances in the aromatic region are doublets and one is a singlet as expected. Two sets of three resonances appear in the alkyl region with the resonances that are shifted downfield being in a 1:2 ratio to those upfield. This is consistent with the fact that one of the rings contains the strongly electron-withdrawing nitro group, while the other two rings remain unchanged and appear similar to the starting material (**5**).

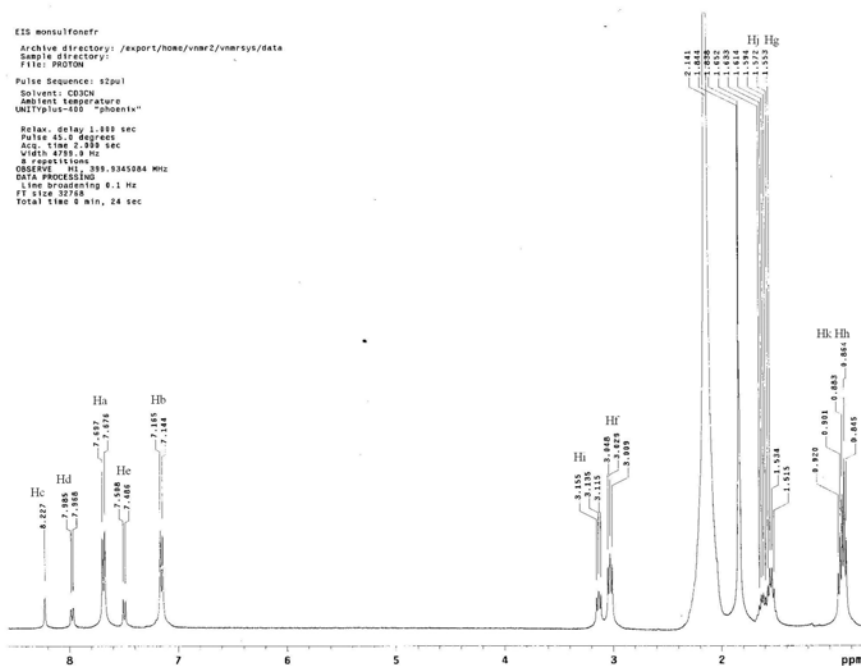
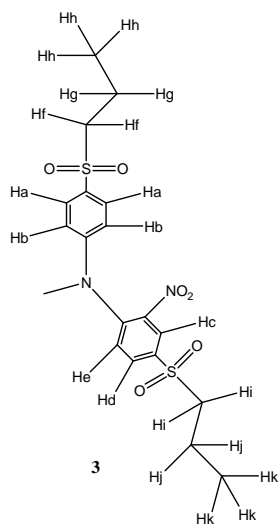


Figure 5 - ¹H NMR spectrum of 4,4',4''-tripropanesulfonyl-2-nitrotriphenylamine (6) with assigned resonances.

The ^{13}C NMR spectrum (Figure 6) further confirms the synthesis of **6**. Three carbons appear in the alkyl region of the spectrum, corresponding to the propyl group bonded to the sulfur. There also appears to be two peaks (within 1ppm of each other) for two of the carbons that are shifted more downfield, as they are more affected by the nitro group. This is consistent with the proton spectrum where the methyl group appears to be less split than the two methylene groups. There are also ten aromatic carbons as expected.

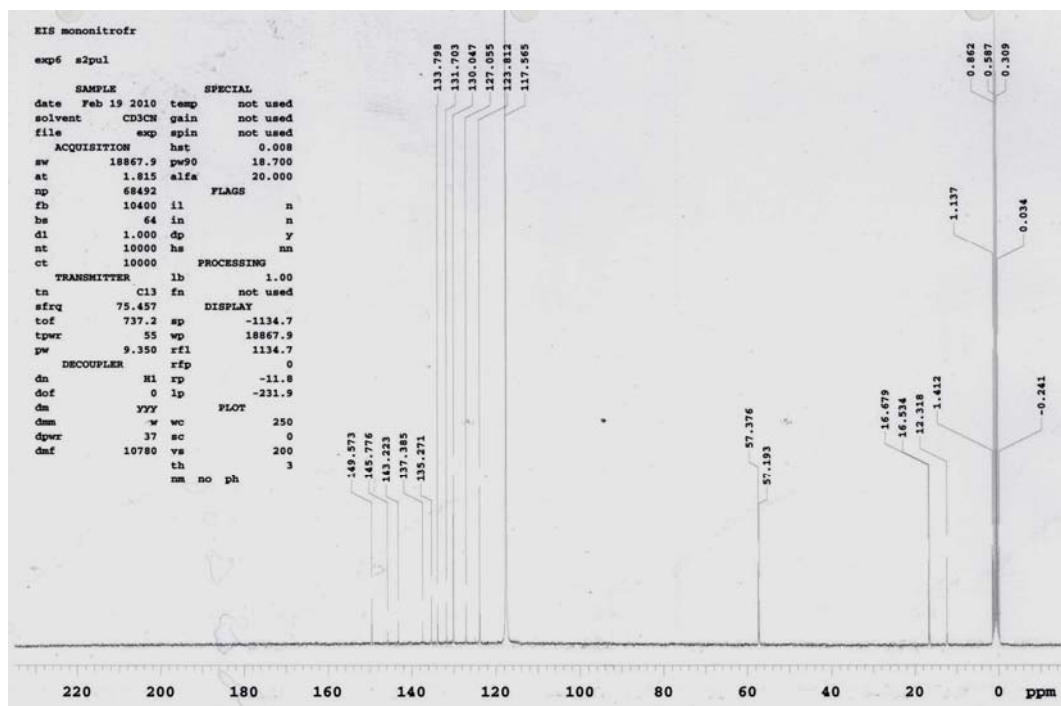


Figure 6 – ^{13}C NMR spectrum of 4,4',4''-tripropanesulfonyl-2-nitrotriphenylamine (**6**)

The COSY spectrum of **6** (Fig. 7) further supports the characterization of the compound. The spectrum confirms that the two large resonances that integrate to 4H (at 7.69 ppm and 7.15 ppm) are coupled with each other and therefore are on the same rings. Coupling between the remaining three aromatic peaks also confirms that those protons are on the same ring and likely correspond to the nitrated ring, as they are shifted downfield.

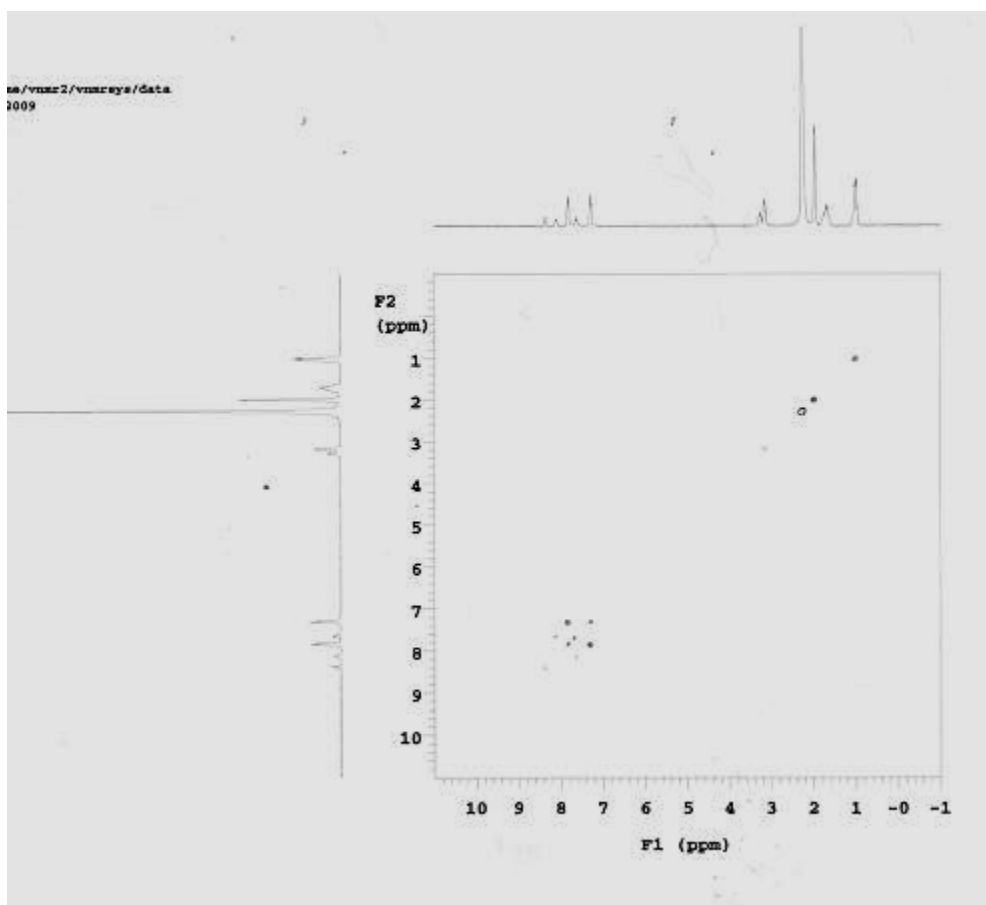


Figure 7 - COSY spectrum of 4,4',4''-tripropanesulfonyl-2-nitrotriphenylamine (**6**)

The ^1NMR spectrum of 4,4',4''-tripropanesulfonyl-2,2'-dinitrotriphenylamine (**7**) is shown below (Figure 8). The five aromatic protons are now integrating in the same ratio to each other, as expected, as there are two protons of each type in the structure. The alkyl protons look similar to those seen in the mono-nitro species (**6**), but this time the set of three that is shifted downfield is in the ratio of 2:1 with those that are upfield. This indicates that two phenyl rings are nitrated. The alkyl protons of the nitrated rings are again shifted more downfield than those on the unnitrated phenyl ring.

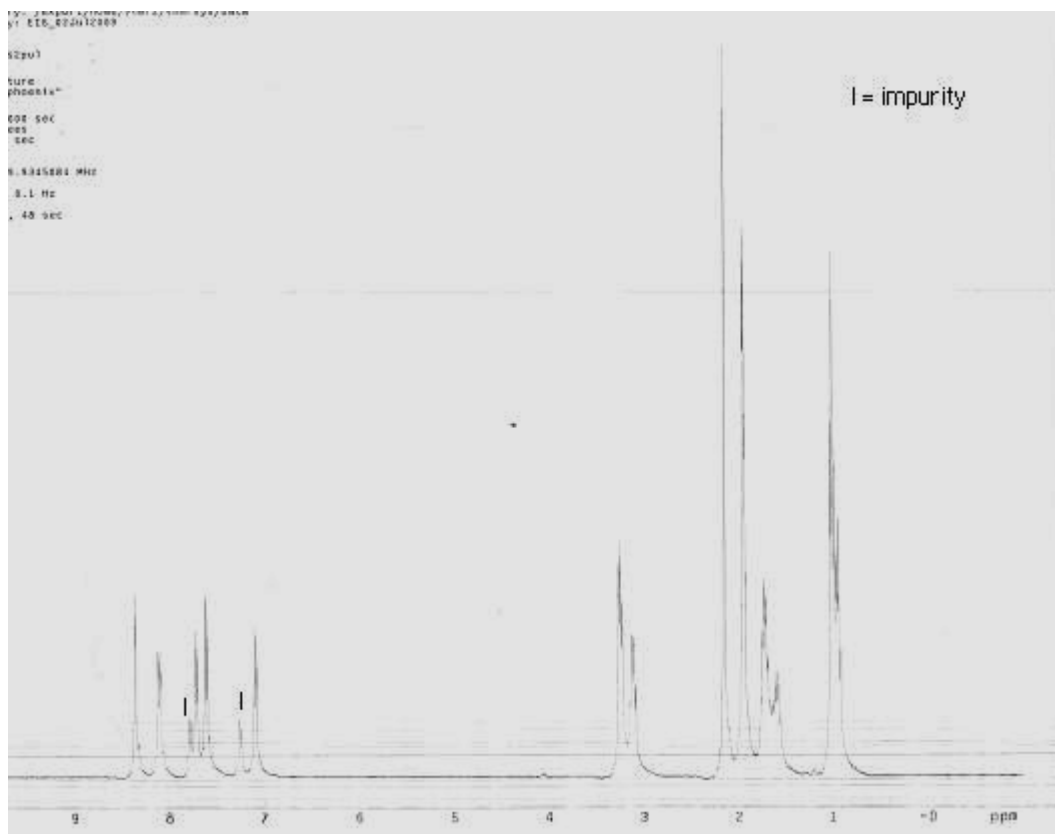


Figure 8 - ^1NMR spectrum of 4,4',4''-tripropanesulfonyl-2,2'-dinitrotriphenylamine (**7**)

The ^{13}C NMR spectrum of 4,4',4''-tripropanesulfonyl-2,2'-dinitrotriphenylamine (**7**) is shown below (Figure 9). Three carbons are located in the alkyl region, as expected with shifts of 57.4, 57.2, 16.7, and 12.3 ppm. The spectrum below only resolved the methylene carbon as distinctly different on the substituted and non-substituted ring, with two peaks within 1 ppm.

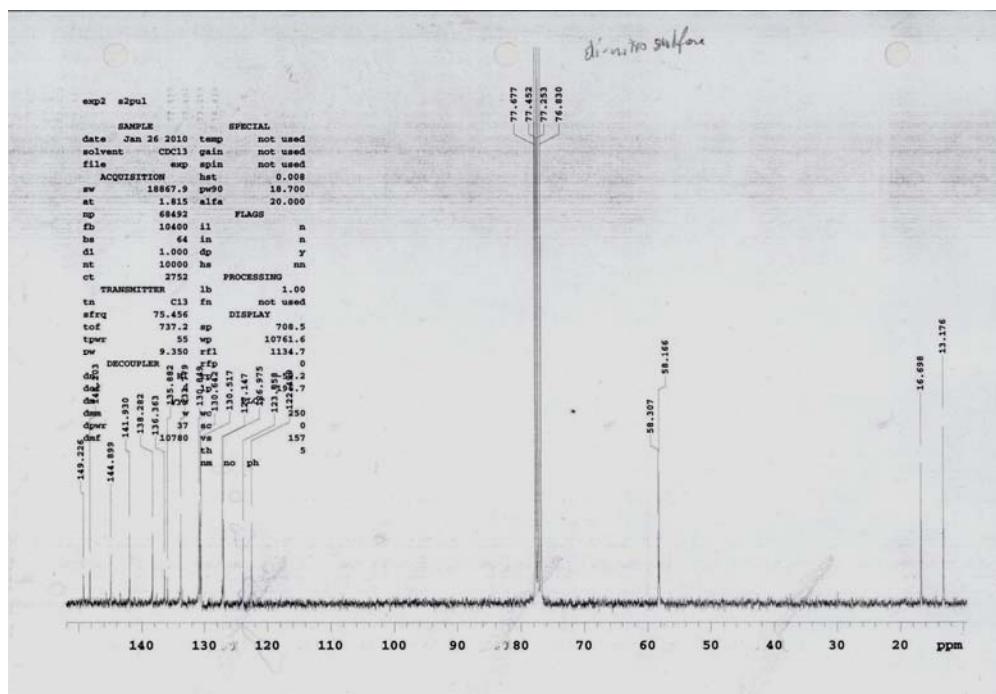


Figure 9 - ^{13}C NMR spectrum of 4,4',4''-tripropanesulfonyl-2,2'-dinitrotriphenylamine (**7**)

The COSY NMR spectrum of 4,4',4''-tripropanesulfonyl-2,2'-dinitrotriphenylamine (**7**) is shown below (Fig. 10). The spectrum shows that all of the alkyl protons couple with their vicinal neighbors as expected and observed in the mono-nitro species (**6**). The aromatic resonances belonging to the unnitrated ring (7.12 ppm, 7.64 ppm) couple with each other. The aromatic resonances belonging to the nitrated ring (7.75, 8.14 ppm) couple with each other. The singlet assigned to the proton in between the NO₂ and the SO₂ is shifted most downfield at 8.39 ppm and was not observed to couple to any protons in the short range as expected.

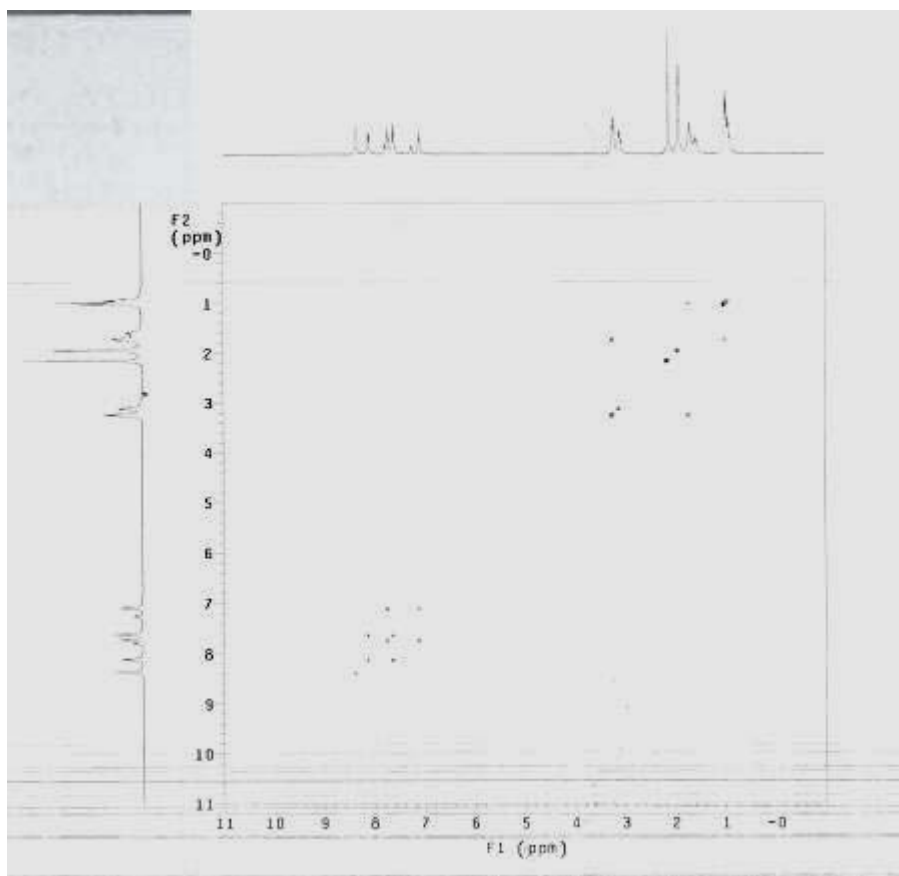


Figure 10 - COSY NMR spectrum of 4,4',4''-tripropanesulfonyl-2,2'-dinitrotriphenylamine (**7**)

RESULTS AND DISCUSSION

A. Cyclic Voltammetry

The oxidation potentials of **6** and **7** are of interest as these compounds are intended to be used as electrocatalysts. Potentials were measured in acetonitrile versus an Ag/AgNO₃ reference electrode using cyclic voltammetry.

The oxidation potential of 4,4',4''-tripropanesulfonyl-2-mononitrotriphenylamine (**6**) was found to be 1.66V. The potential was determined by discerning at which voltage the current observed reaches a peak as seen below (Figure 11).

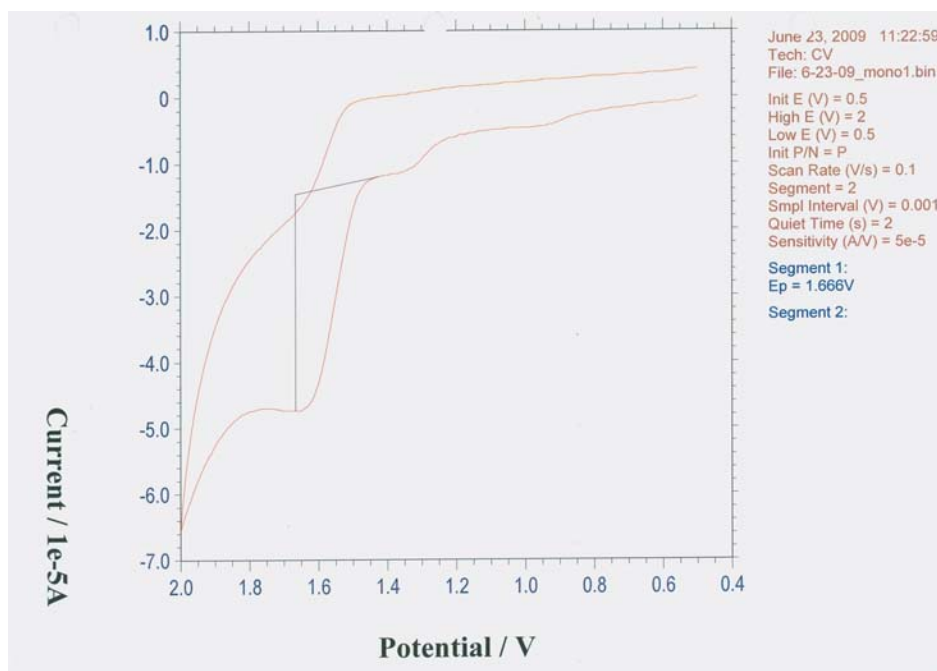


Figure 11 – The voltammogram of 4,4',4''-tripropanesulfonyl-2-mononitrotriphenylamine (**6**)

The voltammogram of 4,4',4''-tripropanesulfonyl-2,2'-dinitrotriphenylamine (**7**) shown below (Fig. 12) did not readily show what the oxidation potential was, as no clear peak was observed. In order to determine the potential, the derivative of the current with respect to potential was obtained.¹⁴

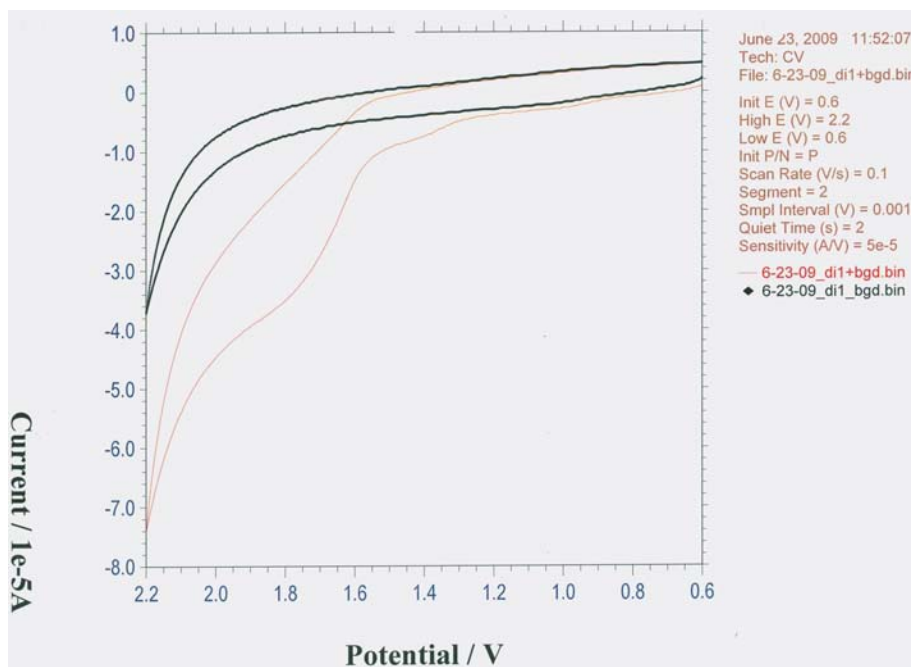


Figure 12 – The voltammogram of 4,4',4''-Tripropanesulfonyl-2,2'-dinitrotriphenylamine (**7**)

The derivative of the voltammogram of 4,4',4''-triopropanesulfonyl-2,2'-dinitrotriphenylamine (**7**) is shown below (Fig. 13). From this diagram, it can be determined that the oxidation potential of **7** is approximately 1.85V.

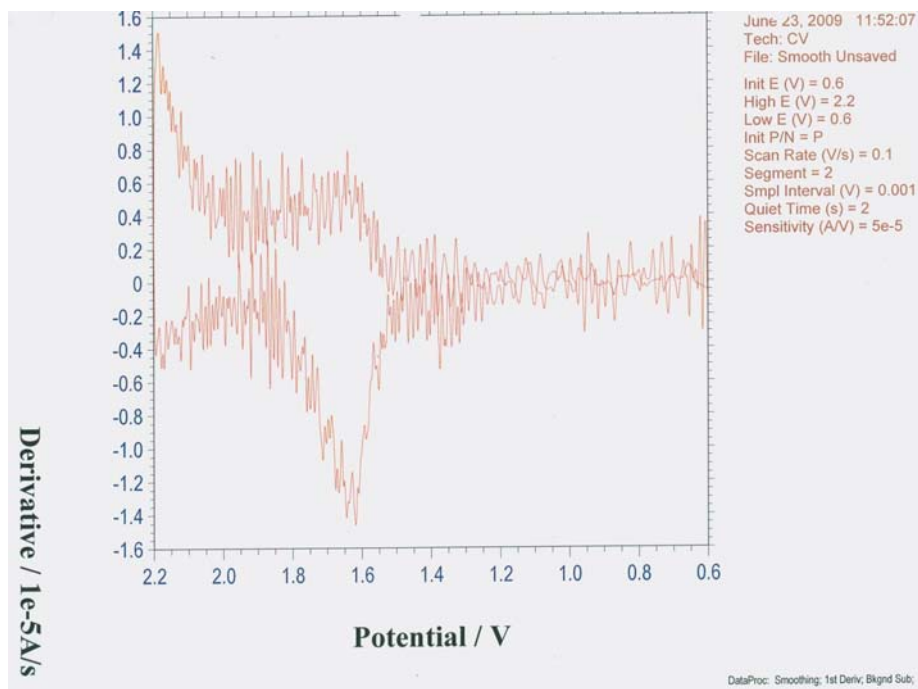


Figure 13 – The derivative of the current with respect to the potential in the voltammogram of 4,4',4''-triopropanesulfonyl-2,2'-dinitrotriphenylamine (**7**)

B. Potential catalytic applications of **6** and **7**

Compounds **6** and **7** have significantly higher oxidation potentials than other triphenylamine compounds synthesized thus far with 1.66V and 1.85V respectively, compared to **5**, which had a potential of 1.15V.⁵ This property makes them attractive as catalysts as they would be able to catalyze reactions involving the anodic oxidation of compounds bearing strong electron withdrawing groups with high oxidation potentials. The 4,4',4''-trichloro-2,2',2''-trinitrotriphenylamine (**3**) catalyst has an oxidation potential of 1.56V, but it proved ineffective due to the chlorine atoms being leaving groups during the electrolyses making the catalyst unstable. This problem should not occur in this compound as sulfinate ions are poor leaving groups. The catalyst should therefore remain stable and relatively nonreactive.

Both **6** and **7** are readily soluble in acetonitrile, which is the most common solvent used for anodic oxidations. The presence of three sulfone groups, the amine, and the nitro group(s) make the compounds quite polar. The propyl groups bonded with the sulfones increase the solubility of the compounds in organic solvents over equivalent compounds bearing methyl groups instead.¹⁵

A major point to consider is the stability of the radical cation that forms during the anodic oxidation reaction. It is important to consider how effective the catalyst will be in becoming regenerated to the non-charged state. The voltammogram (Fig. 11) appears to show that **6** is indeed reversible and has potential to be regenerated a number of times giving it a high turnover rate. The voltammogram of **7** (Fig. 12), however, shows that the di-nitro species may not be as reversible and may result in a lower turnover rate for the catalyst. The electron withdrawing effect of the

nitro group has been considered in the Introduction section, but it is interesting to note what the effect of the sulfone group is on the overall compound. Below (Fig. 14) are a few resonance structures that demonstrate some of the electronegative aspects of the two oxygen bearing functional groups. Structure **A** is likely the major contributor to structure with the most reasonable charge distribution. Computational studies would be able to provide further evidence for this.

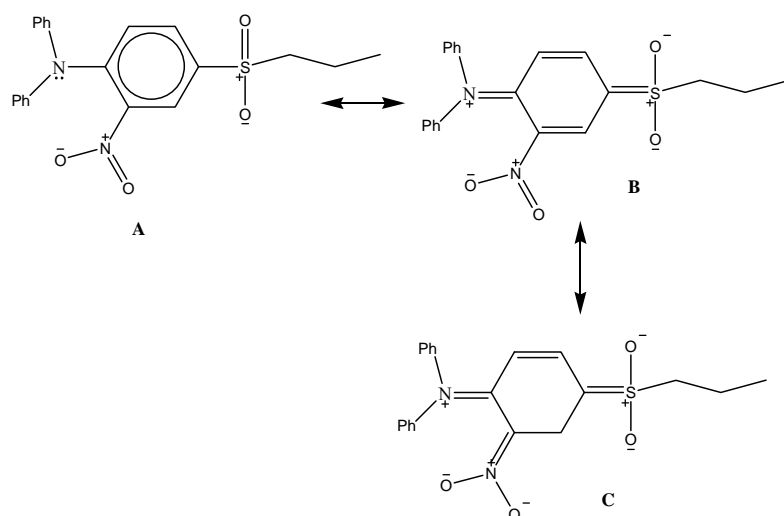


Figure 14 – Possible resonance structures of **6** and **7**.

Below (Fig. 15) are shown the resonance structures of the cation that forms during the electrolysis reactions. Both the sulfone and the nitro group have very strong electron withdrawing properties and are likely to attract the lone electron to some degree as shown.

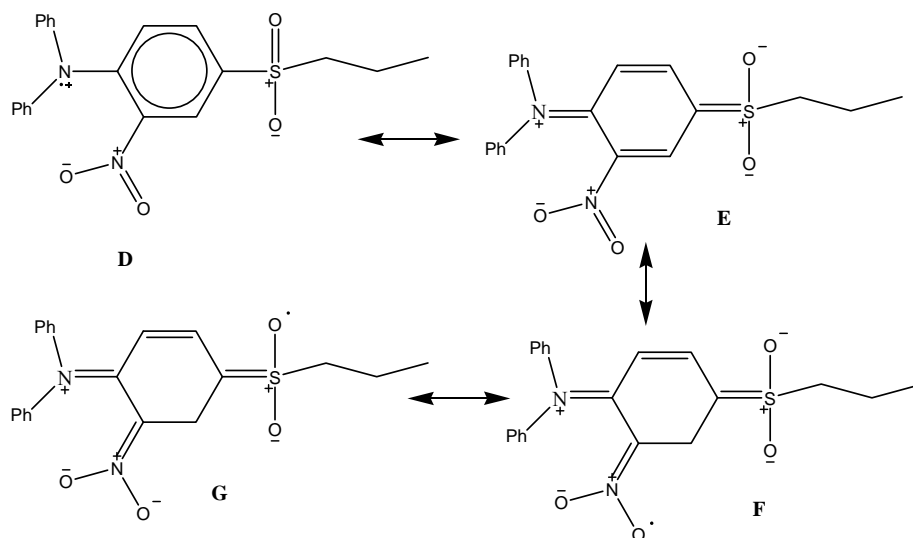


Figure 15 - Possible resonance structures of the radical cation formed in **6** and **7**.

C. Synthetic Considerations

The nitration method of NaNO_2 in trifluoroacetic acid reported by Uemura¹³ is quite effective. With stoichiometric control, either the mono- or the di- species could be produced and the two are easily separated using flash column chromatography. An important step of the reaction is to seal the flask using a rubber septum, which was not originally reported by Uemura,¹³ but was reported later by Wu, X. et. al.⁵ Upon addition of NaNO_2 , the flask contains all the gases inside that are formed. The mechanism presented for the formation of the reactive NO_2^- is presented in Figure 16. A brown gas is seen escaping the flask, which most likely is NO_2 , while NO and N_2O_4 which are colorless gases are also likely present. The loss of these gases

disturbs the mechanism and results in lower yield.

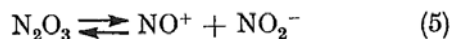
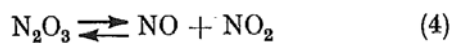
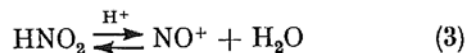
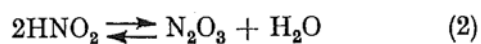


Figure 16 – The proposed mechanism reported by Uemura¹³

The proposed synthesis of 4,4',4''-tripropylthiotriphenylamine **4** only alters the original procedure⁵ by a little bit with a slightly higher temperature, less solvent, and a longer reaction time. Further adjustments in conditions could be attempted to the reaction by changing the temperature, solvent, amount of solvent, time, or the stoichiometric amounts of the main reagent. It should be noted that running the reaction even longer than reported here is likely beneficial, as it decreases the amount of the mono- and di- substituted molecules. This, in turn, would further simplify the purification step and lower the amount of time spent in the preparation of the compound.

The new method to synthesize 4,4',4''-tripropylsulfonyltriphenylamine (**5**) using *m*-CPBA does offer a few advantages over the previously reported method using KHSO₅, commercially available as OXONE®.⁵ First, it uses significantly less solvent, as the starting material is more soluble in CH₂Cl₂, which not only conserves resources, but also makes the workup of the reaction easier and faster as there is less solvent to manage. Second, the reaction time is much shorter and with further study

on how the reaction proceeds should be much shorter than even reported here (6 hours).

EXPERIMENTAL

^1H , COSY, and ^{13}C NMR spectra were measured using Varian Mercury Vx 300MHz pulsed field gradient spectrophotometer and Unity Plus 400MHz pulsed field gradient spectrophotometer. Microanalyses were carried out by Atlantic Microlab Inc., Norcross, GA. Cyclic Voltametry with electronic iR compensation was carried out using CH Instruments (Austin, TX) Model 650-A electrochemistry system.

4,4',4''-tripropylthiotriphenylamine (4). The synthesis was based on the procedure reported by Wu, X, et. al.⁵ Potassium propylmercaptide was prepared by adding 1-propanethiol (5.138g, 67.2 mmol) to a solution of KOt-Bu (7.567g, 67.2 mmol) in MeOH (100 mL). The solvent was removed by rotary evaporation yielding approximately 7.7g of crude material. The mercaptide and 4,4',4''-tribromotriphenylamine (4.67g, 9.7 mmol) were placed in a reaction vessel sealed with a rubber septum and purged with N_2 . DMF (110 mL) was injected into the reaction vessel and the solution was heated to 130°C and stirred for 43 hours. The solvent was removed by rotary evaporation. The residue was dissolved in a 50:50 mixture of CH_2Cl_2 and hexane and the solution was washed with saturated aqueous NH_4Cl and then successively with water and brine, and dried over Na_2SO_4 . Purification by flash chromatography using silica with 3:1 hexanes/ CH_2Cl_2 as the eluent yielded 4,4',4''-tripropanethiotriphenylamine (**4**) (2.7g, 60%): mp 47–49.

4,4',4''-tripropanesulfonyltriphenylamine (5). At 0°C , *m*-chloroperoxybenzoic acid (665mg, 3.85mmol) was added to a solution of 4,4',4''-

tripropanethiotriphenylamine (200mg, 0.43mmol) in 50mL of CH₂Cl₂. The reaction was stirred vigorously for 6 hours in a 100mL round bottom flask on ice.

Approximately 25mL of NaHCO₃ was added to the reaction mixture and stirred for 10 minutes. The organic layer was then washed with H₂O (3 x 30mL) and then dried with Na₂SO₄. The solvent was removed by rotary evaporation. The resulting crude solid was recrystallized from 95% EtOH yielding 4,4',4''-tripropanesulfonyltriphenylamine (**5**) (187mg, 78%).

4,4',4''-tripropanesulfonyl-2-nitrotriphenylamine (6). Nitration was carried out by the procedure of Uemura and coworkers.¹³ At 0-5°C, sodium nitrate (25mg, 0.36mmol) was added to a solution of 4,4',4''-tripropanesulfonyltriphenylamine (200mg, 0.36mmol) in 25mL of trifluoroacetic acid, upon which the solution turned yellow. The mixture was quickly sealed using a rubber septum and stirred for 1 hour at 0-5°C. Approximately 25mL of H₂O was added, followed by the addition of NaOH pellets until the solution was neutralized. The product was extracted with CH₂Cl₂ (4 x 20mL) and washed with H₂O. The organic layer was then dried with Na₂SO₄ and the solvent was removed by rotary evaporation. Purification by flash chromatography using silica with 1:1 ethyl acetate / hexanes, followed by recrystallization in a 4:1 mixture of water to methanol yielded 4,4',4''-tripropanesulfonyl-2-nitrotriphenylamine (**6**). (137mg, 63%): m.p. 156-157°C; ¹H NMR (400MHz, CD₃CN): δ = 8.23 (s, 1H), 7.98 (d, J=6.8Hz, 1H), 7.69 (d, J=8.4Hz, 4H), 7.50 (d, J=8.8Hz, 1H), 7.15 (d, J=8.4Hz, 4H), 3.14 (t, J=8.0Hz, 2H), 3.03 (t, 8.0Hz, 4H), 1.62 (m, J=7.6Hz, 2H), 1.54 (m, J=7.6Hz, 4H), 0.87 (m, J=7.6Hz, 9H). ¹³C NMR

(300MHz, CD₃CN): δ = 149.6, 145.8, 143.2, 137.4, 135.3, 133.8, 131.7, 130.0, 127.1, 123.8, 57.4, 57.2, 16.7, 12.3. Anal. Calcd for C₂₇H₃₂N₂O₈S₃: C, 53.27; H, 5.29. Found: C, 53.14; H, 5.22.

4,4',4''-tripropanesulfonyl-2,2'-dinitrotriphenylamine (7). Nitration was carried out by the procedure of Uemura and coworkers.¹² At room temperature, sodium nitrate (74mg, 1.07mmol) was added to a solution of 4,4',4''-tripropanesulfonyltriphenylamine (202mg, 0.36mmol) in 25mL of trifluoroacetic acid, upon which the solution turned yellow. The mixture was quickly sealed using a rubber septum and stirred for 1 hour. Approximately 25mL of H₂O was added, followed by the addition of NaOH pellets until the solution was neutralized. The product was extracted with CH₂Cl₂ (4 x 20mL) and washed with H₂O. The organic layer was then dried with Na₂SO₄ and the solvent was removed by rotary evaporation. Purification by flash chromatography using silica with 1:1 ethyl acetate / hexanes, followed by recrystallization in a mixture of 4:1 heptane to ethyl acetate yielded 4,4',4''-tripropanesulfonyl-2,2'-dinitrotriphenylamine (**7**). (146 mg, 61%): m.p. 200-202°C; ¹H NMR (400MHz, CD₃CN): δ = 8.39 (s, 2H), 8.14 (d, J=8.4Hz, 2H), 7.81 (d, J=7.5Hz, 2H), 7.64 (d, J=6.9Hz, 2H), 7.12 (d, J=7.5Hz, 2H), 3.26 (t, J=8.4Hz, 4H), 3.14 (m, J=7.5Hz, 2H), 1.74 (m, J=6.9Hz, 4H), 1.64 (m, J=8.1Hz, 2H), 1.00 (m, J=7.5Hz, 9H). ¹³C NMR (300MHz, CDCl₃): δ = 149.2, 148.2, 144.9, 141.9, 138.3, 136.4, 135.9, 133.8, 130.8, 130.6, 130.5, 127.1, 126.9, 123.9, 122.5, 58.3, 58.2, 16.7, 13.2. Anal. Calcd for C₂₇H₃₁N₃O₁₀S₃: C, 49.61; H, 4.78. Found: C, 49.56; H, 4.81.

Cyclic Voltammetry. The cyclic voltammograms of compounds **6** and **7** were measured at a scan rate of 0.1 V/s at a glassy carbon working electrode in a solution of 0.1M LiBF₄ in CH₃CN. The potentials were measured versus Ag/0.1 M AgNO₃ reference electrode.

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