THE SYNTHESIS OF
TETRAAMINO ARYL ETHERS

F. WARREN VILLAESCUSA

JOHN G. BRELAND, JR.

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THE SYNTHESIS OF TETRAAMINO ARYL ETHERS

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John G. Breland, Jr.

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Directorate of Chemical Sciences
Frank J. Seiler Research Laboratory
Air Force Systems Command
U.S. Air Force Academy, Colorado 80840
FOREWORD

This report was prepared by the Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory. The work was initiated under Project No. 7903, "Chemical Synthesis and Characterization," Task No. 7903-01-67, "Monomer Synthesis and Characterization." It was administered under the direction of the Frank J. Seiler Research Laboratory, Air Force Systems Command, U.S. Air Force Academy, Colorado, with Captain John G. Brelan, Jr., serving as administrative principal investigator.

The research described herein represents a portion of the Seiler Laboratory's contribution to a joint project with the Polymers Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson AFB, Ohio. Dr. Fred E. Arnold served as primary AFML/MBP contact and provided invaluable advice and assistance throughout the program.

The report covers work conducted from July 1971 to June 1974. The manuscript was released for publication by the authors in January 1975.

This technical report has been reviewed and is approved.

[Signature]
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Director, Directorate of Chemical Sciences
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ABSTRACT

A general synthesis for the bis(3,4-diaminophenoxy)aryl compounds has been developed. Nucleophilic substitution of 1,2-dinitro-4-fluorobenzene by the sodium salts of aromatic diols produces tetranitro aryl ethers. Catalytic reduction of these compounds in the presence of hydrazine gives the corresponding tetrafunctional amines in good yields.

Polymers utilizing these amines display both good thermal stability and increased solubility in aprotic solvents such as m-cresol.
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SECTION I
INTRODUCTION

The search for polymeric materials having high temperature properties, i.e., the ability to retain their physical and chemical characteristics as well as their dimensional stability at elevated temperatures on the order of 500°C and above, has received constant attention in recent years. The demand for such materials has been greatly accelerated because of their potential usefulness in aerospace applications such as structural adhesives, reinforced plastic composites, high temperature resistant fibers and nose-cones and heat shields for space vehicles.

As a result of their exceptionally high thermal and chemical stability, aromatic heterocyclic polymers such as the polybenzimidazoles (1) or PBI, polyphenylquinoxalines (2) or PPQ, and polyimidazole-imides (with a bis-benzimidazobenzophenanthroline (3) or BBB being an example) have been found to be particularly promising for aerospace applications.\(^1\,^2\)
These polymer systems result from the reaction of amines with carboxylic acids or ketones. Polymerizations in organic solvents, in melts and in polyphosphoric acid (PPA) or similar materials have been used successfully in their synthesis. The final structure of the hetero ring, as well as the type of polymer formed, depends on the starting monomer's composition and geometry.
Being condensation polymers like the nylons and polyimides, the PBI, PPQ and BBB systems give off volatile products (H₂O) during the polymer forming reactions. Also polymerization is often concerted, and controllable, step-wise reaction is not possible. Because of these characteristics, many such materials must be utilized in essentially completely polymerized form with fabrication being accomplished by melting (fusing) the polymer or dissolving it in a suitable solvent system.

Unfortunately, the fused and highly aromatic nature of these systems, which accounts for their exceptional stability, also tends to render them intractable. Physical properties often approach those of brick dust.
with melting points over 500°C and solubilities restricted to strong acids such as sulfuric \((\text{H}_2\text{SO}_4)\) or methane sulfonic \((\text{CH}_3\text{SO}_3\text{H})\). Applications of these types of polymer systems have therefore been essentially restricted to the production of high temperature resistant fibers which can be spun from such acid solutions. This lack of processability has made them of little to no value in the formation of structural adhesives or as matrix resins for composites.

Earlier studies on nylon and polyimide resins\(^3,4\) have revealed that utilization of diamino aryl ether monomers of the general structure (4)

![Chemical Structure](image)

instead of simple benzenoid diamines produced oligomers with significantly increased processability. As the number of ether linkages increased, so did both solubility and fusibility of the resulting resin. Also, the introduction of such linkages did not adversely affect the thermal stability of the resins.

Utilization of similarly structured tetraamines as monomers in the formation of PBI, PPQ and BBB type polymer systems would be expected to produce similar increases in processability. Since the heterocyclic
units in such polymers are formed from the functionality of the monomers during polymerization, use of such modified monomers would not change these basic structures of the polymers. However, the backbone would be modified in two ways. The presence of oxygen (or similar atoms) should markedly increase its solubility in aprotic solvents. Likewise, the inherent flexibility of these linkages should partially destroy the rigidity of the backbone and result in both lower fusing temperatures and increased solubility.

This report describes the development of a general synthesis for the bis(3,4-diaminophenoxy)aryl compounds of the general structure 5 using 1,2-dinitro-4-fluorobenzene (7b) and aromatic diols as starting materials.

By properly selecting the starting diols, a large number of tetraamines possessing specific and unique properties can be produced. The monomers described in this report have been sent to the Air Force Materials Laboratory for polymerization. Initial studies have yielded BBB type polymers which show excellent thermal stability and possess markedly increased solubility in such aprotic solvents as m-cresol.
The general applicability of this synthetic method should allow preparation of numerous new tetraamines suitable for use as monomers in any polymer system requiring \( \omega \)-diamines in the polymer forming reaction(s). When combined with appropriate crosslinking systems, such polymers should find widespread use in the fabrication of both aerospace and commercial items.
The best approach to the desired bis(3,4-diaminophenoxy)aryl compounds (5) was deemed to be via reduction of the corresponding tetranitro compounds. Two possible synthetic routes to these bis(3,4-dinitrophenoxy)aryl compounds (9) are depicted in Schemes I and II.

Scheme I

\[
\begin{align*}
\text{Scheme I} \\
6a & \quad X = \text{Br} \quad 7a & \quad X = \text{Br} \\
_b & \quad X = \text{F} & _b & \quad X = \text{F}
\end{align*}
\]
Ullmann ether syntheses of 1,3-diphenoybenzenes utilizing sodium resorcinate and aryl bromides have been reported. In Scheme I the required aryl bromide would be 1,2-dinitro-4-bromobenzene (7a) which is readily synthesized from m-bromonitrobenzene (6a). Unfortunately, nucleophilic substitution on 7a usually results in replacement of the 2-nitro group instead of the 4-bromo group. This fact was confirmed when 7a was treated with sodium ethoxide in ethanol to produce a nearly quantitative yield of 5-bromo-2-nitrophenetole (10). Therefore the use of 1,2-dinitro-4-bromobenzene (7a) as a precursor to intermediate 9 was abandoned.
Scheme II depicts an attempt to circumvent this problem by the replacement of the labile 2-nitro group in 7a with an amino group. Aromatic nucleophilic substitutions on nitroanilines are known, but go extremely slowly. Hopefully 5-bromo-2-nitroaniline (12a) would still be reactive enough to undergo the required reaction.

m-Bromoaniline (11) was converted in poor yield to 12a by acylation, followed by nitration and hydrolysis of the acetamido group. The yield of 12a was only 27% because of the competing formation of an isomer, 3-bromo-4-nitroaniline (12b), in 33% yield. The subsequent reaction of 12a with sodium ethoxide in ethanol successfully gave 5-ethoxy-2-nitroaniline (13) in 71% yield thus indicating that nucleophilic substitution of the bromo group would take place. However, a successful reaction of 12a with sodium resorcinate to produce the diadduct 14 could not be achieved. Only a few reaction conditions were explored for two reasons; the poor yield of 5-bromo-2-nitroaniline (12a) and the success achieved via Scheme I when 1,2-dinitro-4-fluorobenzene (7b) was used instead of the bromo compound (7a).

The well characterized reaction of 2,4-dinitrofluorobenzene (15) with phenols to produce aryl ether derivatives, including resorcinol to give the diadduct 15b, was modified by employing 1,2-dinitro-4-fluorobenzene (7b). This route was attempted because fluorine is usually more easily displaced than any other group in aromatic nucleophilic substitutions. For instance, Beckwith, Miller and Leahy reported that at 25°C the p-nitrophenoxide anion reacts 2700 times faster with 2,4-dinitrofluorobenzene (15) than with 2,4-dinitrobromobenzene (16). Additionally, Bevan and Bye reported converting 7b into 3,4-dinitroanisole (7c) by treatment with sodium methoxide in methanol at 80°C for 12 hours, although no yields are given.

The starting point for this successful synthesis was m-fluoronitrobenzene (6b) which is commercially available. Nitration by the method of Suschitzky on a large scale gave 1,2-dinitro-4-fluorobenzene (7b) in
60% yield. Suschitzky gave no reason for assuming that the new nitro group is actually para to the fluoro group. However, analysis of the proton and fluorine NMR spectra of the product confirmed it as the desired compound.

Furthest upfield in the proton spectrum (Fig 1) is H-5 as a series of eight lines centered at 7.86 δ with coupling constants of $J_{5,F} = 7.6$ Hz, $J_{5,6} = 9.0$ Hz, and $J_{3,5} = 2.8$ Hz. H-3 appears at 8.34 δ as a doublet of doublets coupled to H-5 and fluorine with $J_{3,F} = 8.0$ Hz. Furthest downfield at 8.45 δ is H-6 as a doublet of doublets split by H-5 and fluorine with $J_{6,F} = 5.0$ Hz. The fluorine spectrum (Fig. 2) consists of six lines centered at 53 ppm downfield from perfluorobenzene with area ratios of 1:1:2:2:1:1. The six lines can only be interpreted to mean that the ortho coupling constants between H-3 and fluorine and between H-5 and fluorine are equal. Different constants would produce eight lines of equal intensity in the spectrum. The value of $J_{3,F}$ and $J_{5,F}$ is 7.2 Hz while $J_{6,F}$ is 4.4 Hz. A comparison of coupling constants from the proton and fluorine spectra is given in Table 1.
Reaction of \( \text{7b} \) with sodium methoxide in methanol at \( 5^\circ\text{C} \) for 1 hour gave a 53% yield of 3,4-dinitroanisole (7c), thus confirming that the fluoro group could be replaced preferentially over the 2-nitro group. Resorcinol (8a) was then chosen as the first aryl diol for the nucleophilic substitution with \( \text{7b} \) and many reaction conditions were tried. Base/solvent systems investigated were triethyl amine/acetone, sodium methoxide/pyridine (cuprous chloride catalyst), and sodium hydride with dimethyl sulfoxide, tetrahydrofuran, diglyme and pyridine as solvents. The sodium hydride/pyridine system gave the best results although sodium hydride/dimethyl sulfoxide was the first system from which the desired product 1,3-bis(3,4-dinitrophenoxy)benzene (9a) was actually isolated. The standard reaction procedure which evolved was to stir under nitrogen a solution of 1,2-dinitro-4-fluorobenzene (7b) in pyridine containing suspended sodium hydride and then add dropwise a solution of the aryl diol (8) in pyridine. After several hours of stirring at room temperature, the reaction mixture was poured into 2N hydrochloric acid. The product was then isolated by either filtration (solid) or extraction (oil or tar). This crude product was further purified by elution chromatography on silica gel columns. Yields of the tetranitro compounds (9) are summarized in Table 2.
TABLE 2
Yields of the Bis(3,4-dinitrophenoxy)aryls

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1,3-Bis(3,4-dinitrophenoxy)benzene</td>
<td>9a</td>
</tr>
<tr>
<td>2,2'-Bis(3,4-dinitrophenoxy)biphenyl</td>
<td>b</td>
</tr>
<tr>
<td>1,5-Bis(3,4-dinitrophenoxy)naphthalene</td>
<td>c</td>
</tr>
<tr>
<td>4,4'-Bis(3,4-dinitrophenoxy)diphenyl sulfide</td>
<td>d</td>
</tr>
<tr>
<td>4,4'-Bis(3,4-dinitrophenoxy)diphenyl sulfone</td>
<td>e</td>
</tr>
</tbody>
</table>

A by-product from the coupling reaction was usually obtained in five to ten percent yield. This was examined in the case of resorcinol (8a) and found to be 1-(3,4-dinitrophenoxy)-3-(2-nitro-5-fluorophenoxy)benzene (17).

Apparently, there was leaving group competition between the fluoro group and the 2-nitro group of 7b. One oxygen of the resorcinate anion would attack the fluoro group on one molecule of 7b and the other oxygen would attack the 2-nitro group on another molecule of 7b thus giving the observed by-product (17). No 1,3-bis(2-nitro-5-fluorophenoxy)benzene (18) was ever isolated. That is there did not appear to be any significant amount of substitution where both oxygens of the resorcinate attacked the 2-nitro group of 1,2-dinitro-4-fluorobenzene (7b).
The structure shown for 17 was assumed to be the most likely because the 2-nitro group is more labile than the 1-nitro group. Replacement of the 1-nitro group would result in

![Chemical structure](image)

The proton magnetic resonance spectrum (Fig 3) confirmed the by-product structure as 17. The proton on the fluorine containing ring that would be furthest downfield in both 17 and 19 is H-3. This is due to the presence of the ortho nitro group. Expected patterns for these two protons, using coupling constants obtained from the spectrum of 7b (Fig 1), are shown in Figure 4. The spectrum for the by-product has an absorption overlapping that of H-5 on the dinitrophenoxy ring. The pattern of this proton agrees with the expected pattern for H-3 of compound 17.

Reduction of the tetranitro compound 9a to 1,3-bis(3,4-diaminophenoxy) benzene (5a) proved difficult. Several procedures were tried without success. Each time thin layer chromatography showed several products. Procedures which were attempted included catalytic hydrogenation over platinum oxide (in several solvents); stannous chloride in hydrochloric acid and sodium hydrosulfite in dimethylacetamide.

A successful procedure was developed using hydrazine hydrate in ethanol with palladium on charcoal as a catalyst. With this technique, compound 5a could be isolated but was found to decompose either upon standing or during attempted recrystallization. It was necessary to purify and
Figure 3

H_1 NMR

EXPECTED \( J_{3,4} = 2 \text{ Hz} \)
\( J_{3,F} = 5 \text{ Hz} \)

OBSERVED \( J_{3,4} = 10 \text{ Hz} \)
\( J_{3,F} = 6 \text{ Hz} \)

Figure 4

\[ J_{3,F} = 5 \text{ Hz} \]
\[ J_{3,3} = 2.5 \text{ Hz} \]
\[ J_{3,4} = 9 \text{ Hz} \]

17
19
store it as the tetrahydrochloride derivative. The other tetraamino compounds (5b-e) were found to be much more stable and could be handled as the free amines. Thus 9a had been an unfortunate choice as the first tetranitro compound to be reduced. The unsuccessful reduction procedures described above may have failed only because 5a is unstable. However, these procedures were not attempted on the remaining tetranitro compounds (9b-e) because of the success of the hydrazine hydrate reduction.

The general procedure which evolved was to heat to reflux an ethanolic solution of the tetranitro compound (9) containing an amount of suspended 10% palladium on charcoal equal to ten percent by weight of the tetranitro compound. To this solution was added dropwise an ethanolic solution of one ml of hydrazine hydrate for each millimole of tetranitro compound. After the solution was heated at reflux for several hours, it was suction filtered through Celite filter aid into stirred, cold, concentrated hydrochloric acid. The precipitate which consisted of tetraamine hydrochloride and hydrazine hydrochloride was collected, partially dried, dissolved in water and made basic with concentrated ammonium hydroxide solution. The insoluble tetraamine was then separated from the aqueous phase containing the soluble hydrazine and recrystallized from an appropriate solvent. Yields of the various tetraamines (5) are given in Table 3.

**TABLE 3**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1,3-Bis(3,4-diaminophenoxy)benzene</td>
<td>5a</td>
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<td>2,2'-Bis(3,4-diaminophenoxy)biphenyl</td>
<td>b</td>
</tr>
<tr>
<td>1,5-Bis(3,4-diaminophenoxy)naphthalene</td>
<td>c</td>
</tr>
<tr>
<td>4,4'-Bis(3,4-diaminophenoxy)diphenyl sulfide</td>
<td>d</td>
</tr>
<tr>
<td>4,4'-Bis(3,4-diaminophenoxy)diphenyl sulfone</td>
<td>e</td>
</tr>
</tbody>
</table>

*As the tetrahydrochloride
Both the tetraamino (5) and tetranitro (9) compounds were unusually stable in the mass spectrometer. In all but one case (compound 9a) the parent peak was also the base peak. Very few fragments had relative intensities greater than 10% of the molecular ion and these are reported in the experimental section. Proton nuclear magnetic resonance spectra of these compounds are discussed in the appendix.

No polymerization reactions were attempted at FJSRL. Samples of the tetraamines (5a-e) were sent to AFML where polymers of the imidazole-imide (BBB) type were produced by reacting the tetraamines with 1,4,5,8-naphthalene-tetracarboxylic acid (20) and/or 4,4'-dinaphthalic acid dianhydride (21).

These initial polymerization attempts produced materials which were soluble in aprotic solvents (such as m-cresol) and which possessed intrinsic viscosities [n] as high as .8 as determined in methane sulfonic acid. Thermogravimetric analysis (TGA) showed stabilities up to 10% weight loss at 650°C in nitrogen and 540°C in air. Further and more complete studies of polymer systems utilizing amines of the type described in this report will be undertaken by AFML. Initial polymerization studies are described in AFML-TR-74-279. 1
SECTION III
EXPERIMENTAL

General: All common solvents were reagent grade except hexane which was J.T. Baker practical grade. Pyridine was dried and stored over molecular sieves. The following material was used as obtained from the sources indicated: sodium hydride (57% dispersion in mineral oil), Alfa Products; m-fluoronitrobenzene, Pierce Chemical Co.; 4,4'-dihydroxydiphenyl sulfone, Monsanto Corporation; 4,4'-dihydroxydiphenyl sulfide, Crown-Zellerbach Corporation; hydrazine hydrate (99%), J.T. Baker; palladium on charcoal (10%), Matheson Coleman and Bell; resorcinol, o,o'-biphenol and 1,5-naphthalamenediol, all from Aldrich Chemical Co. Solvent extracts of aqueous solutions were dried over anhydrous magnesium sulfate. Solvents were removed on a Buchi Rotavapor. Melting points were determined on a Kofler melting point apparatus and are uncorrected. Elemental microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Chromatography: Elution chromatography columns were prepared using a slurry of silica gel (J.T. Baker, 60-200 mesh) in hexane. The mixture to be chromatographed was dissolved in a suitable solvent (methylene chloride if possible) and silica gel (10-20% of the weight used for the column) was added. Removal of the solvent gave a silica-gel powder coated with the mixture. Addition of this powder to the column's top gave a uniform band of absorbed material.

Spectra: All spectra were determined by Mr. J. Lloyd Pflug, FJSRL, as follows:

mass spectra using a DuPont Instrument Type 21-491 Double Focusing Mass Spectrometer. The ionizing potential was 78 eV; the ionizing current was 250-300μA; the accelerating potential was 1100 volts coupled with an electric sector voltage of 100 volts. The sample was introduced from a glass capillary into the mass spectrometer with a heated direct insertion probe. The mass spectra were recorded via a CEC 5-124A recording oscillograph.
proton magnetic resonance spectra using either a Varian Model A-60 or T-60A Nuclear Magnetic Resonance Spectrometer with $d_6$-DMSO solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported under the $\delta$ convention in ppm relative to TMS (0 ppm).

fluorine 19 magnetic resonance spectra using a Varian Model T-60A Nuclear Magnetic Resonance Spectrometer with $d_6$-DMSO solvent and perfluorobenzene as an internal standard. Chemical shifts are reported in Hz relative to perfluorobenzene.

1,2-Dinitro-4-fluorobenzene (7b). To a stirred solution of concentrated nitric acid (400 ml) and concentrated sulfuric acid (400 ml) was added m-fluoronitrobenzene (6b) (100 g, 0.71 moles) dropwise over a period of 30 min. The solution was then heated at 70°C for 1½ hours, cooled to 30°C and poured into a 4000 ml beaker one-half full of crushed ice. Enough ice was added to bring the volume to 3500 ml and the suspension was stirred mechanically for 15 min. The bright yellow solid was collected and washed by mechanically stirring with water (1 Z), saturated sodium carbonate solution (3 x 1 l) and water (1 l). Yield of pale yellow crude product after vacuum drying (35°C, 25 mm Hg, 16 hours) was 97.0 g (73%). Recrystallization (with charcoal treatment) from 95% ethanol (200 ml) yielded 73.4 g (56%) of 1,2-dinitro-4-fluorobenzene (7b). mp 51-3°C (lit. 1055-6°C). A second crop of 5.5 g (4%), mp 50-1°C, was obtained by removal of the mother liquor and recrystallization of the yellow residue from 95% ethanol (40 ml).

Pmr: $\delta$ ($d_6$-DMSO), 8.45 (doublet of doublets, 1 proton, H-6, $J_{5,6} = 9.0$ Hz, $J_{6,F} = 5.0$ Hz), 8.34 (doublet of doublets, 1 proton, H-3, $J_{3,5} = 2.8$ Hz, $J_{3,F} = 8.0$ Hz), 7.85 (doublet of doublets, 1 proton, H-5, $J_{5,F} = 7.6$ Hz).

Mass Spectrum: m/e (%), 186 M⁺ (100), 94 (29), 93 (10), 82 (49), 81 (19), 74 (10), 63 (17), 57 (11), 50 (17), 46 (10).
3,4-Dinitroanisole (7c). To a stirred solution of sodium methoxide in methanol (0.15 g sodium, 10 ml methanol) under nitrogen at -5°C was added dropwise a solution of 1,2-dinitro-4-fluorobenzene (7b) (0.50 g, 2.70 mmole). The reaction mixture was stirred 1 hour, poured into water (50 ml) and extracted with chloroform (3 x 20 ml). The combined extracts were washed with 1N hydrochloric acid (25 ml), saturated sodium bicarbonate solution (25 ml), and saturated sodium chloride solution (25 ml), dried and the solvent removed to yield a yellow solid. Recrystallization from ethanol afforded 0.37 g of 3,4-dinitroanisole (7c) as white needles: mp 70-71°C (lit. 14, 70°C).

Pmr: δ (d₆-DMSO), 4.00 (singlet, 3 protons, -CH₃), 7.41 (doublet of doublets, 1 proton, H-6), 7.78 (doublet, 1 proton, H-2, J₂,₆ = 3 Hz), 8.28 (doublet, 1 proton, H-5, J₅,₆ = 9 Hz).

1,3-Bis(3,4-dinitrophenoxo)benzene (9a). To a stirred suspension of sodium hydride (3.4 g oil dispersion, 0.081 mole) in dry pyridine (200 ml) under nitrogen was added resorcinol (8a) (4.4 g, 0.040 mole). The resulting sodium resorcinate suspension was stirred for 1/2 hr, cooled to -5°C and solid 1,2-dinitro-4-fluorobenzene (7b) (22.0 g, 0.118 mole) was added all at once. The reaction mixture was stirred 2 1/2 hr at -5°C and poured into 2N hydrochloric acid (400 ml) at 0°C. The liquid was decanted from the yellow tar which formed and extracted with chloroform (3 x 100 ml). The combined extracts were used to dissolve the yellow tar and then washed with 2N hydrochloric acid (2 x 50 ml), saturated sodium bicarbonate solution (3 x 50 ml), water (50 ml) and saturated sodium chloride solution (50 ml). The extract was dried and the solvent removed to produce 20 g of red tar which was chromatographed on silica gel (320 g) by elution with hexane-benzene mixtures. Yields in the following order from the column were 1,2-dinitro-4-fluorobenzene (7b), 6.72 g; 1- (3,4-dinitrophenoxo)-3-(2-nitro-5-fluorophenoxo)benzene (17), 1.90 g; and the desired product, 1,3-bis(3,4-dinitrophenoxo)benzene (9a), 9.39 g (53%). Recrystallization of 9a from ethanol (700 ml) yielded 8.48 g (48%) of pale yellow solid: mp 106-8.5°C. A small portion was recrystallized twice more from ethanol to afford an analytical sample: mp 107-8.5°C.
2,2'-Bis(3,4-dinitrophenoxy)biphenyl (9b). To a stirred solution of 1,2-dinitro-4-fluorobenzene (7b) (17.2 g, 0.093 mole) in pyridine (200 ml) containing suspended sodium hydride (6.3 g oil dispersion, 0.15 mole) was added dropwise over a period of 45 min. a solution of o,o'-biphenol (8b) (8.6 g, 0.046 mole) in pyridine (50 ml) under nitrogen. Reaction temperature was kept below 40°C by periodic use of an ice bath. The reaction mixture was stirred at room temperature for 15 hr, poured into 2N hydrochloric acid (800 ml) and stirred mechanically for 1 hr. The resulting aqueous suspension was extracted with methylene chloride (3 x 150 ml). The combined extracts were washed with 2N hydrochloric acid (4 x 100 ml), water (100 ml), and saturated sodium chloride (100 ml), dried, and the solvent removed to yield 26.3 g of red oil. Chromatography on silica gel (260 g) by elution with hexane-benzene mixtures yielded 16.2 g (67%) of 2,2'-bis(3,4-dinitrophenoxy)biphenyl (9b). Recrystallization of a small portion from cyclohexene-benzene afforded an analytical sample: mp 128.5-130°C.

Pmr: δ (d₆-DMSO), 8.15 (doublet, 2 protons, H-5 on dinitrophenoxy rings, J₅,₆ = 9 Hz), 7.57 (doublet, 2 protons, H-2 on dinitrophenoxy rings, J₂,₆ = 2.7 Hz), 7.50-7.31 (complex multiplet, 8 protons, biphenyl rings), 7.18 (doublet of doublets, 2 protons, H-6 on dinitrophenoxy rings).

Mass Spectrum: m/e (%), 518 M⁺ (100), 168 (90).

Anal. Calcd for C₂₄H₁₄N₄O₁₀ (518.4): C, 55.61; H, 2.72; N, 10.81.
Found: C, 55.58; H, 2.78; N, 10.73.
1,5-Bis(3,4-dinitrophenoxy)naphthalene (9c). To a stirred suspension of sodium hydride (1.68 g oil dispersion) in dry pyridine (100 ml) was added 1,5-naphthalenediol (8c) (3.20 g, 0.020 mole). The reaction mixture was heated for 1 hr at 50°C under nitrogen, chilled to -2°C and 1,2-dinitro-4-fluorobenzene (7b) (11.20 g, 0.060 moles) was added all at once. After stirring 3 hours at -5°C, the solution was poured into 2N hydrochloric acid (500 ml) and the brown precipitate collected, washed with water, and vacuum dried (20 mm Hg, 70°C, 17 hrs) to yield 10.7 g pale brown solid. The crude product was dissolved in boiling tetrahydrofuran (900 ml), treated with charcoal, filtered, and the volume reduced to 350 ml. The solution was reheated to boiling and 95 percent ethanol (200 ml) added slowly. Storage at -15°C for 18 hours produced 6.22 g (63%) of 1,5-bis(3,4-dinitrophenoxy)naphthalene (9c) as a yellow solid: mp 224-8°C. A small portion was recrystallized several times from tetrahydrofuran-ethanol to produce an analytical sample: mp 231-2°C.

Pmr: δ (d6-DMSO), 8.32 (doublet, 2 protons, H-5 on dinitrophenoxyl rings, J5,6 = 9.0 Hz), 8.00 (doublet, 2 protons, H-2 on dinitrophenoxyl rings, J2,6 = 2.7 Hz), 7.91-7.56 (complex multiplet, 6 protons, naphthalene ring), 7.41 (doublet of doublets, 2 protons, H-6 on dinitrophenoxyl rings).

Mass Spectrum: m/e (%), 492 M+ (100), 400 (11).

Found: C, 54.09; H, 2.35; N, 11.21.

4,4'-Bis(3,4-dinitrophenoxy)diphenyl sulfide (9d). To a stirred solution of 1,2-dinitro-4-fluorobenzene (7b) (7.44 g, 0.040 mole) in dry pyridine (200 ml) containing suspended sodium hydride (2.2 g oil dispersion, 0.052 mole) was added dropwise over a period of 30 min a solution of 4,4'-dihydroxydiphenyl sulfide (8d) (4.35 g, 0.020 mole) in dry pyridine (50 ml) under nitrogen. Reaction temperature was kept below 25°C by periodic use of an ice bath. The reaction mixture was stirred at room temperature for 17 hr, poured into 2N hydrochloric acid (1 l) and stirred mechanically.
for 1 hr. The liquid was decanted and the residual red tar taken up in methylene chloride (500 ml). The resulting solution was washed with 2N hydrochloric acid (3 x 100 ml) & saturated sodium chloride solution (100 ml), decolorized (Norit charcoal), dried, and the solvent removed to yield 11.2 g orange oil. Chromatography twice on silica gel (first column 200 g, second column 310 g) by elution with hexane-benzene mixtures followed by recrystallization from benzene yielded 6.07 g (55%) of 4,4'-bis(3,4-dinitrophenoxy)diphenyl sulfide (9d): mp 132-134°C.

Pmr: δ (d₆-DMSO), 8.40 (doublet, 2 protons, H-5 on dinitrophenoxy rings, J₅,₆ = 9.0 Hz), 7.87 (doublet, 2 protons, H-2 on dinitrophenoxy rings, J₂,₆ = 2.7 Hz), 7.70-7.20 (complex multiplet, 10 protons).

Mass Spectrum: m/e (%), 550 M⁺ (100), 291 (10).

Anal. Calcd for C₂₄H₁₄N₄O₁₀S (550.5): C, 52.38; H, 2.56; N, 10.18; S, 5.83.

Found: C, 52.47; H, 2.50; N, 10.11; S, 5.94.

4,4'-Bis(3,4-dinitrophenoxy)diphenyl sulfone (9e). To a stirred solution of 1,2-dinitro-4-fluorobenzene (Tb) (7.50 g, 0.040 mole) in dry pyridine (200 ml) containing suspended sodium hydride (2.20 g oil dispersion, 0.052 mole) was added dropwise over a period of 25 min a solution of 4,4'-dihydroxydiphenyl sulfone (8e) (5.0 g, 0.020 mole) in dry pyridine (50 ml) under nitrogen. The reaction mixture was stirred 18 hours, poured into 2N hydrochloric acid (1 l) and stirred 2 hr. The resulting red tar was dissolved in methylene chloride (300 ml), filtered, and washed with 2N hydrochloric acid (4 x 100 ml) & saturated sodium chloride solution (100 ml), dried, and the solvent removed to yield 10.37 g of yellow solid. Chromatography three times on silica gel (each column 200 g) by elution with hexane-acetone mixtures produced 5.76 g (50%) of a yellow solid, mp 180-93°C. Recrystallization from acetone-hexane afforded 4.16 g (36%) of 4,4'-bis-(3,4-dinitrophenoxy)diphenyl sulfone (9e): mp 192-6°C. Several recrystallizations from acetone-hexane gave an analytical sample: mp 197-8.5°C.
Pmr: δ (d$_6$-DMSO), 8.37 (doublet, 2 protons, H-5 on dinitrophenoxy rings, $J_{5,6} = 9.0$ Hz), 8.17 (doublet, 4 protons, ortho to -SO$_2^-$, $J_{o,m} = 9.0$ Hz), 8.06 (doublet, 2 p, H-2 on dinitrophenoxy rings, $J_{2,6} = 2.7$ Hz), 7.60 (doublet of doublets, 2 protons, H-6 on dinitrophenoxy rings), 7.51 (doublet, 4 protons, meta to -SO$_2^-$).

Mass Spectrum: m/e (%), 582 M$^+$ (100), 492 (19), 307 (67), 275 (28), 140 (43).

Anal. Calcd for C$_{24}$H$_{14}$N$_4$O$_{12}$S (582.5): C, 49.49; H, 2.42; N, 9.62; S, 5.50.

Found: C, 49.60; H, 2.40; N, 9.52; S, 5.65.

1,3-Bis(3,4-diaminophenoxy)benzene tetrahydrochloride (5a tetrahydrochloride). A stirred suspension of 1,3-bis(3,4-dinitrophenoxy)benzene (9a) (7.0 g, 0.016 mole) in absolute ethanol (600 ml) was heated under reflux for 1-hour with nitrogen bubbling below the liquid surface. Heating was stopped and, after boiling had subsided, palladium on charcoal (10%, 0.80 g) was added followed by dropwise addition of hydrazine hydrate (16 ml). The reaction mixture was heated under reflux for 3 hours, cooled to 70°C, and suction filtered through Celite filter aid under nitrogen. The solvent was removed to produce the tetraamine as a brown solid which was dissolved in tetrahydrofuran (200 ml) followed by addition of concentrated hydrochloric acid (200 ml). The resulting purple precipitate was collected and, while still wet, dissolved in water (100 ml), heated with Norit charcoal, and filtered. Addition of concentrated hydrochloric acid (200 ml) and storage overnight at -15°C yielded 4.68 g (62%) of 1,3-bis(3,4-diaminophenoxy)-benzene tetrahydrochloride (5a tetrahydrochloride) as a pink solid: mp 232-236°C.

Pmr: δ (D$_2$O), 6.48-6.92 (complex multiplet, 7 protons, all H ortho to oxygen), 7.25 (two superimposed doublets, 3 protons).

Mass Spectrum: m/e (%), 322 M$^+$ (free amine) (100), 216 (35), 162 (16), 161 (11), 124 (10), 123 (24), 104 (13), 95 (19), 44 (23).
2,2'-Bis(3,4-diaminophenoxy)biphenyl (Sb). A stirred solution of 2,2'-bis(3,4-dinitrophenoxy)biphenyl (9b) (22.0 g, 0.0425 mole) in absolute ethanol (500 ml) containing suspended palladium on charcoal (10%, 2.2 g) was heated to reflux under nitrogen, and a solution of hydrazine hydrate (43 ml) in ethanol (100 ml) was added dropwise over a period of 40 min. The reaction mixture was heated at reflux for 17 hours, chilled in an ice bath, and suction filtered through Celite filter aid into stirred, cold, concentrated hydrochloric acid (1 l). The resulting precipitate of hydrazine hydrochloride and the desired tetr'amine hydrochloride was collected, partially dried, and dissolved in water (1 l). Concentrated ammonium hydroxide solution (300 ml) was added and the resulting precipitate collected and vacuum dried to yield 14.9 g (88%) of 2,2'-bis(3,4-diaminophenoxy)biphenyl (Sb). A small portion was recrystallized from ethanol-water to provide an analytical sample: mp 172-4°C.

Pmr: δ (d<sub>6</sub>-DMSO), 5.68-6.60 (complex multiplet, 12 protons, -NH<sub>2</sub> and H-2 to H-6 on phenoxy rings), 6.73 (doublet, 2 protons, H-5 on diaminophenoxy rings, J<sub>5,6</sub> = 8.5 Hz), 6.80 (doublet of doublets, 2 protons, H-3 on biphenyl ring, J<sub>3,4</sub> = 8.0 Hz, J<sub>3,5</sub> = 2.0 Hz), 7.00-7.50 (complex multiplet, 6 protons, H-4, 5,6 on biphenyl ring). Pmr with D<sub>2</sub>O added, 6.73-7.43 (as above), 6.03 (doublet of doublets, 2 protons, H-6 on phenoxy rings, J<sub>5,6</sub> = 8.5 Hz, J<sub>2,6</sub> = 2.5 Hz), 6.30 (doublet, 2 protons, H-2 on phenoxy rings).

Mass Spectrum: m/e (%), 398 M<sup>+</sup> (100).

Anal. Calcd for C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub> (398.5): C, 72.34; H, 5.57; N, 14.06.

Found: C, 72.12; H, 5.42; N, 13.83.
1,5-Bis(3,4-diaminophenoxy)naphthalene (5c). A stirred solution of 1,5-bis(3,4-dinitrophenoxy)naphthalene (9c) (6.0 g, 12.2 mmole) in absolute ethanol containing suspended palladium on charcoal (10%, 0.60 g) was heated to reflux under nitrogen. A solution of hydrazine hydrate (8 ml) in ethanol (30 ml) was added dropwise over a period of 40 min. The reaction mixture was heated at reflux for 6 hrs, chilled in an ice bath, and suction filtered through Celite filter aid into stirred, cold concentrated hydrochloric acid (1 l). The resulting precipitate of hydrazine hydrochloride and the desired tetraamino hydrochloride was collected, partially dried, and dissolved in water (300 ml). Concentrated ammonium hydroxide solution (60 ml) was added and the resulting precipitate collected and vacuum dried to produce 4.5 g (90%) of the desired 1,5-bis-(3,4-diaminophenoxy)naphthalene (5c). Recrystallization from benzene afforded an analytical sample as white needles: mp 230-231°C.

\[ \text{Pmr: } \delta (d_6-DMSO), 6.25 \text{ (doublet of doublets, 2 protons, } J_{5,6} = 8 \text{ Hz, } J_{2,6} = 2.5 \text{ Hz, } H-6 \text{ on phenoxy rings}), 6.39 \text{ (doublet, 2 protons, } H-2 \text{ on phenoxy rings}), 6.61 \text{ (doublet, 2 protons, } H-5 \text{ on phenoxy rings}), 6.85 \text{ (doublet, 2 protons, } H-2, 6 \text{ on naphthalene nucleus, } J_{2,3} \text{ and } J_{6,7} = 8 \text{ Hz), 7.44 \text{ (doublet of doublets, 2 protons, } H-3, 7 \text{ on naphthalene nucleus, } J_{2,3}, J_{3,4}, J_{6,7} \text{ and } J_{7,8} = 8 \text{ Hz), 7.93 (doublet, 2 protons, } H-4, 8 \text{ on naphthalene nucleus).} \]

\[ \text{Mass Spectrum: } m/e (\%), 372 M^+ (100), 186 (5). \]
\[ \text{Anal.: Calcd for } C_{22}H_{20}N_4O_2 (372): \text{ C, 70.94; H, 5.41; N, 14.46. Found: C, 71.30; H, 5.40; N, 14.37.} \]

1,5-Bis(3,4-diacetamidophenoxy)naphthalene (5c) tetraacetate). To a mixture of pyridine (50 ml) and acetic anhydride (25 ml) was added crude 1,5-bis(3,4-diaminophenoxy)naphthalene (5c) (0.69 g, 1.85 mmole). After 10 min., a precipitate started to form and after 30 min the mixture was chilled in an ice bath and filtered. The precipitate was washed with water and vacuum dried to yield 0.70 g of pale brown solid. Recrystallization from dimethyl sulfoxide gave 0.51 g (51%) of 1,5-bis(3,4-diacetamidophenoxy)naphthalene (22): mp 270-3°C. A second recrystallization afforded
0.30 g of an analytical sample as white micro needles: mp 274-8°C.

Pmr: δ (d\textsubscript{6}-DMSO), 2.10 (singlet, 12 protons, -COCH\textsubscript{3}), 6.82-7.20 (complex multiplet, 4 protons, H-2, 5 on naphthalene nucleus and H-6 on phenoxy rings), 7.45-7.72 (complex multiplet, 6 protons, H-3, 4,7,8 on naphthalene nucleus and H-2 on phenoxy rings), 8.00 (doublet, 2 protons, H-5 on phenoxy rings, J\textsubscript{5,6} = 8 Hz), 9.39 (broad, 4 protons, N-H).

Mass Spectrum: m/e (%), 480 M\textsuperscript{+}-60 (1), 462 (1), 420M\textsuperscript{+}-20 (100), 403 (2), 272 (10), 44 (10), 44 (10), 43 (8), 42 (10), 41 (5).

Anal. Calcd for C\textsubscript{30}H\textsubscript{28}N\textsubscript{4}O\textsubscript{6}: C, 66.67; H, 5.22; N, 10.36.

Found: C, 66.28; H, 5.25; N, 9.94.

4,4'-Bis(3,4-diaminophenoxy)diphenyl sulfide (5d). A stirred solution of 4,4'-bis(3,4-dinitrophenoxy)diphenyl sulfide (9d) (1.00 g, 1.82 mmoles) in absolute ethanol (25 ml) containing suspended palladium on charcoal (10%, 0.10 g) was heated to reflux under nitrogen and a solution of hydrazine hydrate (2.4 ml) in absolute ethanol (5 ml) was added dropwise. The reaction mixture was heated at reflux for 24 hours and then suction filtered while hot to remove the catalyst. Evaporation of the liquid gave the crude tetraamine as a brown solid. Recrystallization from ethanol-water yielded 0.45 g (58%) of 4,4'-bis(3,4-diaminophenoxy)diphenyl sulfide (5d), as brown plates, mp 123-132°C. A second recrystallization afforded 0.29 g as an analytical sample: mp 127-135°C.

Pmr: δ (d\textsubscript{6}-DMSO), 4.46 (broad, 8 protons, -NH\textsubscript{2}), 6.15 (doublet of doublets, 2 protons, H-6 on dianimophenoxy rings, J\textsubscript{2,6} = 2.5 Hz, J\textsubscript{5,6} = 8.0 Hz), 6.32 (doublet, 2 protons, H-2 on dianimophenoxy rings), 6.58 (doublet, 2 protons, H-5 on dianimophenoxy rings), 6.90 (doublet, 4 protons meta to -S-, J\textsubscript{0,m} = 9 Hz), 7.31 (doublet, 4 protons, ortho to -S-).

Mass Spectrum: m/e (%), 430 M\textsuperscript{+} (100), 415 (25), 324 (43).

Anal. Calcd for C\textsubscript{24}H\textsubscript{22}O\textsubscript{2}N\textsubscript{4}S (430.5): C, 66.96; H, 5.15; N, 13.01; S, 7.45.

Found: C, 66.84; H, 5.20; N, 12.91; S, 7.30.
4,4''-Bis(3,4-diaminophenoxy)diphenyl sulfone (5e). A stirred solution of 4,4''-bis(3,4-dinitrophenox)ydiphenyl sulfone (9e) (1.6 g, 2.74 mmoles) in absolute ethanol (150 ml) containing suspended palladium on charcoal (10%, 0.15 g) was heated to reflux under nitrogen. A solution of hydrazine hydrate (5 ml) in absolute ethanol (30 ml) was added drop-wise over a period of 10 min. The reaction mixture was heated at reflux for 16 hours, chilled in an ice bath, and suction filtered through Celite filter aid into stirred, cold, concentrated hydrochloric acid (300 ml). The resulting precipitate of hydrazine hydrochloride and the tetraamino hydrochloride was collected, vacuum dried, and dissolved in water (100 ml). Addition of concentrated ammonium hydroxide (15 ml) produced 0.80 g (63%) of 4,4''-bis(3,4-diaminophenoxy)diphenyl sulfone (5e) as a brown solid: mp 105-110°C. 

Pmr: δ (d6-DMSO), 4.75 (broad multiplet, 8 protons, NH2), 6.15 (doublet of doublets, 2 protons, H-6 on dianino phenox rings, J2,6 = 2.5 Hz, J5,6 = 8.0 Hz), 6.31 (doublet, 2 protons, H-2 on dianino phenox rings), 6.60 (doublet, 2 protons, H-5 on dianino phenox rings), 7.00 (doublet, 4 protons, meta to -SO2-, J0,m = 9 Hz), 7.85 (doublet, 4 protons, ortho to -SO2-).

Mass Spectrum: m/e (%), 462 M+ (100), 356 (22).

Anal.: Calcd for C24H22N4O4S (462.5): C, 62.32; H, 4.79; N, 12.11; S, 6.93.

Found: C, 61.95; H, 4.30; N, 11.92; S, 6.54.

1-(3,4-Dinitrophenox)-3-(2-nitro-5-fluorophenox)benzene (17). Obtained 1.90 g as a tarry by-product from the synthesis of 1,3-bis(3,4-dinitrophenox)benzene (9a). The tar was dissolved in hot ethanol (60 ml), precipitated by sudden chilling in a dry ice-acetone bath, and collected. Upon warming to room temperature the solid became a tar. Solidification took place after standing for about 3 weeks to yield 1.75 g (10%) of 1-(3,4-dinitrophenox)-3-(2-nitro-5-fluorophenox)benzene (17): mp 73.5°C.
Pmr: $\delta$ ($d_6$-DMSO), 8.32 (doublet, 1 proton, H-5 on dinitro-phenoxy ring, $J = 9$ Hz), 8.25 (doublet of doublets, 1 proton, H-3 on nitrofluorophenoxy ring, $J_{3,4} = 10$ Hz, $J_{3,F} = 6$ Hz), 7.96 (doublet, 1 proton H-2 on dinitrophenoxy ring, $J_{2,6} = 2.5$ Hz), 7.75 - 7.05 (complex multiplet, 7 protons).

**Mass Spectrum:** m/e (%), 415 M$^+$ (26), 186 (12), 140 (100), 96 (10), 75 (10).

**Anal.:** Calcd for C$_{18}$H$_{10}$O$_8$N$_3$F (415.3): C, 52.06; H, 2.29; N, 10.12; F, 4.57.

**Found:** C, 51.96; H, 2.29; N, 9.98; F, 4.69.

5-Bromo-2-nitroaniline (12a). To a stirred solution of m-bromoaniline (11a) (39.4 g, 0.229 mole) in water (625 ml) and concentrated hydrochloric acid (25 ml) was added all at once acetic anhydride (33 ml) followed immediately by a solution of anhydrous sodium acetate (25 g) in water (125 ml). The mixture was stirred 30 min and the solid collected, washed with water and vacuum dried to yield 44.4 g (90%) of m-bromoacetanilide, mp 87-89°C. To a stirred solution of the m-bromoacetanilide (39.3 g, 0.182 mole) in glacial acetic acid (80 ml) and concentrated sulfuric acid (60 ml) at 40°C was added dropwise concentrated nitric acid (25 ml). Reaction temperature rose to 55°C. Stirring was continued and the temperature maintained above 40°C for 4 hours after which the reaction mixture was poured into ice and neutralized with concentrated sodium hydroxide solution. The resulting dark red solid was collected and vacuum dried to yield 41.4 g of crude nitrated m-bromoacetanilide. This material was hydrolyzed at 95°C with 60% sulfuric acid (350 ml), poured into ice and made basic with concentrated sodium hydroxide solution. The resulting solid was collected and vacuum dried to give 28.0 g of crude product. Chromatography on silica gel (420 g) by elution with benzene, chloroform and ethyl acetate afforded 10.6 g (27%) of the desired 5-bromo-2-nitroaniline (12a). Recrystallization from ethanol gave 7.03 g: mp 157-5°C (lit. 151-5°C). A second crop of 2.01 g was also obtained.
Pmr: $\delta$ (d$_6$-DMSO), 6.80 (doublet of doublets, 1 proton, H-4).
7.35 (doublet, 1 proton, H-6, $J_{4,6} = 2$ Hz), 7.58 (broad, 2 protons, -NH$_2$),
7.96 (doublet, 1 proton, H-3, $J_{3,4} = 9$ Hz).

The chromatography column also yielded 13.0 g (33%) of an undesired isomer 3-bromo-4-nitroaniline (12b). Recrystallization from ethanol afforded 10.8 g: mp 175-8°C (lit.$^{16}$ 175-6°C).

Pmr: $\delta$ (d$_6$-DMSO), 6.70 (doublet of doublets, 1 proton, H-6),
6.80 (broad, 2 protons, -NH$_2$), 7.03 (doublet, 1 proton, H-2, $J_{2,6} = 2$ Hz,
8.03 (doublet, 1 proton, H-5, $J_{5,6} = 9$ Hz).

5-Ethoxy-2-nitroaniline (13). To a stirred solution of sodium ethoxide (0.30 g of sodium, 10 ml absolute ethanol) heated to reflux under nitrogen was added dropwise a solution of 5-bromo-2-nitroaniline (12a) (0.20 g, 0.92 mmole) in absolute ethanol (20 ml). After 22 hours the solvent was removed and the red residue mixed with water (10 ml) and extracted with chloroform (1 x 10 ml, 2 x 5 ml). The combined extracts were washed with water (10 ml) & saturated sodium chloride solution (10 ml), dried and the solvent removed to yield 0.14 g of 5-ethoxy-2-nitroaniline (13). Purification by preparative layer chromatography (silica gel, 20 x 20 x 0.2 cm, 9/1 benzene-ethyl acetate) followed by recrystallization from ethanol afforded 0.12 g (71%): mp 107-8°C (lit.$^{17}$ 105-6°C).

Pmr: $\delta$(d$_6$-DMSO), 1.39 (triplet, 3 protons, -CH$_3$, $J = 7$ Hz),
4.11 (quartet, 2 protons - CH$_2$-), 6.29 (doublet of doublets, 1 proton, H-4),
6.54 (doublet, 1 proton, H-6, $J_{4,6} = 2.5$ Hz), 7.99 (doublet, 1 proton, H-3
$J_{3,4} = 9.5$ Hz).

5-Bromo-2-nitrophenetole (10). To a stirred solution of sodium ethoxide in absolute ethanol (0.37 g sodium in 13 ml ethanol) was added dropwise under nitrogen a solution of 4-bromo-1,2-dinitrobenzene (7a)(0.50 g, 2.0 mmol) in absolute ethanol (10 ml). The reaction mixture was stirred 1 hour, poured into water (50 ml) and extracted with chloroform (3 x 25 ml). The combined extracts were washed with 2N hydrochloric acid (25 ml),
saturated sodium bicarbonate solution (25 ml) & saturated sodium chloride solution (25 ml), dried, and the solvent removed to yield an off-white solid (0.49 g). Chromatography on silica gel (30 g) by elution with hexane-benzene mixtures followed by recrystallization from ethanol gave 0.28 g of 5-bromo-2-nitrophenetole (10) as pale yellow plates: mp 79-81°C (lit. 6b, 79.5-80.5°C).

\[ \delta (\text{DMSO}, d_6), 1.37 \text{ (triplet, 3 protons, } -\text{CH}_3, J = 7 \text{ Hz)}, 4.30 \text{ (quartet, 2 protons, } -\text{CH}_2-, J = 7 \text{ Hz)}, 7.34 \text{ (doublet of doublets, 1 proton, } H-4), 7.65 \text{ (doublet, 1 proton, } H-6, J_{4,6} = 2 \text{ Hz}), 7.90 \text{ (doublet, 1 proton, } H-3, J_{3,4} = 8.5 \text{ Hz}). \]

**Mass Spectrum:** m/e (%), 245/247 M⁺ (51), 217/219 (100), 201/203 (20), 187/189 (40), 184 (17), 161/159 (25), 145/143 (18), 75 (16), 63 (65).
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16. Beilstein, 12, II, 403.
PART I: Proton NMR of the Bis(3,4-dinitrophenoxy)aryls (9) and the Bis(3,4-diaminophenoxy)aryls (5)

The protons on the dinitrophenoxy rings in the bis(3,4-dinitrophenoxy)aryl compounds were easily distinguished in the proton magnetic resonance spectra of these compounds. Chemical shifts of the three protons were different enough that simple first order splitting resulted. The protons of the Ar portion usually gave complex patterns.

\[
\begin{align*}
\text{Table 4 summarizes the chemical shifts and coupling constants of the dinitrophenoxy portion of 9.}
\end{align*}
\]

\[
\begin{array}{cccccc}
\text{Compound} & \text{Chemical Shift (δ)} & \text{Coupling Constant (Hz)} \\
& H-2 & H-5 & H-6 & J_{2,6} & J_{5,6} \\
\hline
9a & 7.96 & 8.35 & 7.59 & 2.7 & 9.0 \\
b & 7.57 & 8.15 & 7.18 & 2.7 & 9.0 \\
c & 8.00 & 8.32 & 7.41 & 2.7 & 9.0 \\
d & 7.87 & 8.40 & (1) & 2.7 & 9.0 \\
e & 8.06 & 8.37 & 7.60 & 2.7 & 9.0 \\
\end{array}
\]

(1) Could not be distinguished from protons on -Ar-. 

34
In the bis(3,4-diaminophenoxy)aryl compounds (5) first order coupling was also obtained for the protons on the diaminophenoxy rings. Table 5 summarizes the chemical shifts and coupling constants of the diaminophenoxy portion of the molecules.

Table 5

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (δ)</th>
<th>Coupling Constant (Hz)</th>
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<tr>
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<tr>
<td>b</td>
<td>6.30</td>
<td>6.73</td>
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<tr>
<td>e</td>
<td>6.31</td>
<td>6.60</td>
</tr>
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</table>

(1) As the tetrahydrochloride in D₂O

(2) Could not be distinguished from the -Ar- protons

PART II. Spectra

Nuclear magnetic resonance spectra of the major compounds in this report will be printed as a FJSRL Technical Memorandum. Copies will be available upon request to interested persons.
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17. **DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)**

18. **SUPPLEMENTARY NOTES**  
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19. **KEY WORDS (Continue on reverse side if necessary and identify by block number)**  
   Tetraamine  
   Monomer  
   Benzimidazobenzophenanthroline  
   Oxyarylene  
   Thermally stable

20. **ABSTRACT (Continue on reverse side if necessary and identify by block number)**  
   A general synthesis for the bis(3,4-diaminophenoxy)aryl compounds has been developed. Nucleophilic substitution of 1,2-dinitro-4-fluorobenzene by the sodium salts of aromatic diols produce tetranitro aryl ethers. Catalytic reduction of these compounds in the presence of hydrazine give the corresponding tetrafunctional amines in good yields. Polymers utilizing these oxyaryleneamines display both good thermal stability and increased solubility in aprotic solvents such as m-cresol.