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"Starburst" polyarylamines and their semiconducting complexes as potentially electroactive materials

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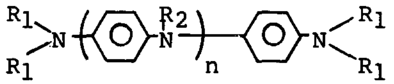
Summary

Highly branched "starburst" polyarylamines were synthesized by repetitive condensations of 2,4-dinitrofluorobenzene with anilines, followed by reduction. These starburst arylamines were complexed with iodine to form semiconducting products. The reduced arylamines were examined by cyclic voltammetry.

Introduction

Electroactive organic materials are of current interest. Oxidation ("doping") of electron-rich aromatic compounds such as triarylamines has led to ion-radical conducting salts(1).

Linear arylamines have been reported by Honzl and coworkers(2,3) through nucleophilic aromatic substitution on p-nitrochlorobenzene by aniline, followed by reduction, or by oxidative condensation. They prepared linear oligoarylamines up to tetramers. The iodine and perchlorate complexes of these amines had conductivities in the semi-conducting region (10^{-7} to 10^{-1} $^{-1}$ cm^{-1}).



R_1 = H, CH_3

R_2 = H, CH_3

n = 1 to 3

Tomalia and coworkers have recently offered the novel concept of the "starburst" polymer(4,5). Here progressive dendritic branching leads by stepwise reactions to highly branched polymer molecules. Tomalia's report was confined to polyamides and to polyethyleneimines.

Honzl's synthesis had been difficult because p-nitrohalobenzenes are not highly reactive with aryl amines, and cooxidation routes led to mixtures of products. In contrast, 2,4-dinitroaryl halides, especially the fluoride, are far more reactive(6). Moreover, dimethyl sulfoxide is a particularly effective solvent for these reactions(7). Accordingly, it seemed appropriate to build starburst aromatic amines through stepwise condensations of 2,4-dinitrofluorobenzene with aniline derivatives, followed by reduction, and to investigate the electrical properties of the derived complexes.

Results

As the initial aromatic amine, four aniline derivatives were selected. A coding system was devised to simplify the description of these complex molecules. Here, "a" is addition and "r" is reduction. Each initial aromatic amine has its own code designation: A = aniline, PDA = p-phenylenediamine, ADPA = N-phenyl-p-phenylenediamine, DADPA = 4,4'-diaminodiphenyl-amine. A material designated $PDAa^2r^2$ means a polyarylamine based on p-phenylenediamine which has been subjected to two cycles of reaction with 2,4-dinitrofluorobenzene (2,4-DNFB) and two reductions (Scheme I).

The condensations proceeded well in DMSO at room temperature. Some reactions were exothermic. Overall yields were high.

The multinitro amines were insoluble in water or ethanol, but were soluble in DMSO. At the second round of addition they became less soluble and difficult to crystallize, owing perhaps to their increasingly disordered structures. Their internal donor-acceptor character may contribute to insolubility.

The polyamines were insoluble in water, but were soluble in alcohol, acetonitrile or DMSO. At the second round of reductions they were very sensitive to autooxidation and were not crystalline.

Finally, the polyamines became unstable toward air or light oxidation. For these reasons, we terminated our growth at the third stage of monomer additions. This contrasts with the compounds studied by Tomalia (4), which remained tractable during the structural buildup.

The yields and melting points of the starburst arylamines are collected in Table I. The data on the chemically oxidized compounds of the polyarylamines prepared are collected in Table II. The complexes were difficult, if not impossible to crystallize. Conductivity of pressed pellets as high as $10^{-5}\,\Omega^{-1}cm^{-1}$ was observed.

It was thought that electrochemical oxidation methods would give more defined complexes. These would have more regular, definable structure, and perhaps higher conductivities.

Cyclic voltammetry was done to determine if electrochemical oxidation was feasible. The results are tabulated in Table II. Due to the complexity of amine oxidation, in general, and multiplicities of the cyclic voltammograms, electrooxidation techniques could not be applied, and were deemed unuseful.

In conclusion, the idea that "starburst" arylamines would yield highly semi-conductive redox complexes was tested. The trend of longer chain length giving higher conductivity as found by Honzl does not apply, due to the complexity of the aromatic structures, and resulting inability to form crystalline complexes.

Scheme 1
Synthesis of PDAa^{2}r^2

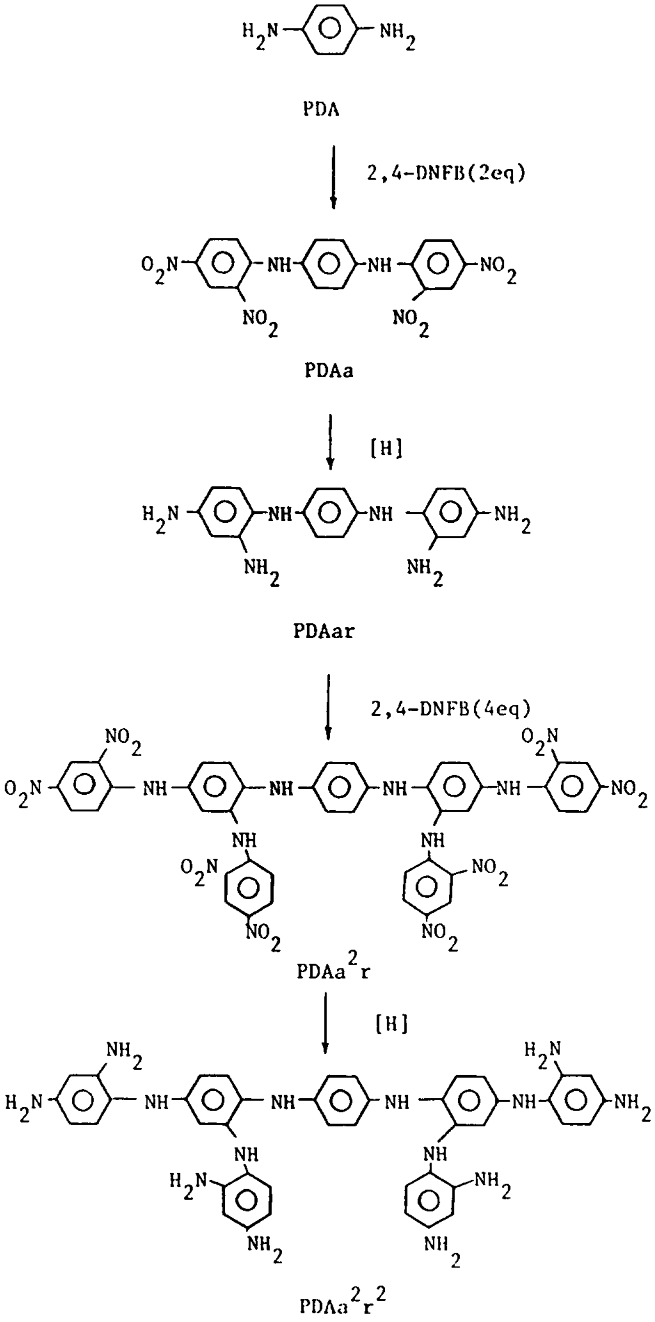


Table I
Syntheses and Properties of Starburst Polyarylamines[b]

Base (N)		N-a^1	N-a^1r^1	N-a^2r^1	N-a^2r^2
A	Yield	90.7%	95.2%	86.3%	93.8%
	Mp	154-155°C[a] needles(EtOH)	126-127°C[a]	180-185°C[a]	100-110°C viscous oil
ADPA	Yield	94.5%	87.9%	77.5%	86.7%
	Mp	150-152°C[a] plates(EtOH)	128-131°C[a]	105°C[a](oil)	90°-softens 100°-starts to flow
PDA	Yield	89.7%	89.7%	78.7%	57.9%
	Mp	272-273°C[a] red plates (DMSO)	236-240°C[a] 245°C (dec)	180°C(dec)[a]	--
DADPA	Yield	98%	82.7%	68.5%	--
	Mp	252-254°C[a]	200-206°C (dec)	150°C[a](oil)	

[a] Satisfactory elemental analysis was obtained.

[b] All compounds soluble in DMSO, insoluble in H_2O; nitro compounds were insoluble, and amines were soluble in ethanol.

Table II

Cyclic Voltammetry and Electrical Conductivity of Starburst Arylamine Complexes[a]

Compounds	Cyclic Voltametry [b] Reversible Oxidation Potential(s)	Iodine Complexes Iodine Ratio	Conductivity[c]
Aar	0.2, 0.48, 0.87	---	----
Aa^2r^2	0.69	1:1	$<10^{-8}$
		1:2	1.9×10^{-6}
ADPAar	0.21, 0.65	1:1	1.0×10^{-6}
		1:2	1.2×10^{-6}
$ADPAa^2r^2$	1.18	1:1	1.3×10^{-7}
		1:2	5.6×10^{-7}
PDAar	0.16, 0.40	1:1	2.6×10^{-6}
		1:2	2.3×10^{-6}
$PDAa^2r^2$	0.27, 0.45, 0.63	1:0.5	2.0×10^{-6}
		1:1	5.7×10^{-6}
DADPAar	0.24, 0.67, 1.27	1:1	1.5×10^{-5}

[a] See Experimental for conditions [b] Volts [c] $(\text{ohm-cm})^{-1}$

Experimental

Methods - IR spectra were recorded using KBr disks and a Perkin-Elmer 983 spectrophotometer.

NMR spectra were recorded on a Varian EM 360 60 MHz Spectrometer.

Melting points were uncorrected and obtained on a Mel-Temp Laboratory device or a Hoover Capillary Melting Point Apparatus.

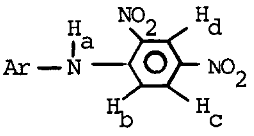
Hydrogenation was carried out in a Parr Pressure reaction Apparatus.

All elemental analyses (C,H,N) were performed by MicAnal, Tucson, Arizona.

Sources of Materials - Aniline (A) was supplied by Mallinckrodt, Inc. and was distilled to a colorless oil before use, 42.5°C (0.25 mm Hg). Aldrich supplied p-phenylenediamine (PDA), N-phenyl-p-phenylenediamine (ADPA), and 4,4'-diaminodiphenylamine (DADPA). The PDA was used unpurified in most cases with satisfactory results. ADPA was purified by recrystallization from alcohol to give pale white needles, mp 63-65°C. DADPA was generated in situ from 4,4'-diaminodiphenylamine sulfate (tech 85%). 2,4-Dinitrofluorobenzene (Aldrich 99%) was used without additional purification.

Typical Addition - In a 150 ml erlenmeyer flask is placed the amine (0.01 mole) in DMSO (20-35 ml). 2,4-DNFB (0.011 mole per eq. NH_2) is added slowly with stirring. Solvent was not used for compound Aa, and 2eq. of amine was used to eliminate HF. An exothermic reaction takes place. The solution is stirred for an additional 2-3 hours and added to a precipitating medium. Precipitation was best accomplished as follows: ADPAar, H_2O; ADPAa^{2}r, i-PrOH; PDAa, Et_2O; and DADPAa, H_2O. The precipitate is collected by filtration washed with copious amounts of ethanol and then soxhlet extracted (ethanol). The material is dried in vacuo to give the desired 2,4-dinitrophenyl derivative.

NMR (DMSO) :



H_a - 9.8 to 10.1 ppm broad singlet
H_b - 7.5 to 8.5 ppm broad singlet
H_c - 8.2 to 8.4 ppm doublet of doublets
H_d - 8.7 to 8.9 ppm doublet

Typical Reduction - In a 250 ml pressure bottle are placed the 2,4-dinitrophenyl compound (0.01 mole), acetonitrile (100ml) and 10% by weight of 10% Pd on carbon. The bottle is attached to a Parr Pressure Reaction Apparatus and flushed 3 times with hydrogen to remove Oxygen. The reaction vessel is pressurized to approximately 40 psi and the mixture is hydrogenated until the pressure remains constant (approx. 1 psi = 0.004 mmole nitro). Reduction of Na compounds takes 1-4 hours; reduction of Na^{2}r compounds takes 1-2 days. If the polyamine remains soluble, the solution is filtered through celite, and the solvent is quickly stripped off via rota-evaporation. Further purification was not necessary in these cases.

NMR (DMSO) : 4.8-5.4 (br s, -NH_2), 6.0-7.8 (br m, ArNH and aromatic), ppm.

Iodine Complexes - In separate beakers are placed 1-2.5 mmoles of the amine in 15 ml acetonitrile and the equivalent amount of iodine in 15 ml acetonitrile. When the solutions become homogeneous, they are mixed and allowed to stir 1-4 hours. The precipitated complex (if any), is filtered, and the solvent evaporated. Precipitated complexes and those remaining in solution showed identical conductivities. The complex is completely dried in vacuo at 25^{o}C before further measurements. No iodine sublimes during drying.

Conductivity Measurements - The conductivities of the polyamine complexes were obtained via a four probe method developed by Van der Pauw(8) for small discs of uniform thickness. Pellets were pressed on a Carver Laboratory Press at 17,000 psi in a Beckmann KB-01 IR pellet maker. The pellets were cemented to the four-point probe using Electrodag 502.

Standards for calibration were used. A germanium sliver (0.20 cm) was connected to the probe to give a conductivity of $1.4X10^{-2}\ \Omega^{-1}cm^{-1}$ (lit(9) $2.1X10^{-2}\ \Omega^{-1}cm^{-1}$). A tellurium sliver gave a conductivity of $1.97\ \Omega^{-1}cm^{-1}$ (lit(9) $2.29\ \Omega^{-1}cm^{-1}$).

Cyclic Voltammetry - A BAS CV-1B Cyclic Voltammogram was used. The solvent was acetonitrile and the supporting electrolyte was tetrabutylammonium tetrafluoroborate. The scan speed was 300 mV/sec.

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