per million (ppm) relative to tetramethylsilane (Me_4Si) as an internal standard for proton spectra and benzotrifluoride (BTF) as an external standard for fluorine spectra. Gas chromatography was performed with a Varian Model 3700 gas chromatograph and a 10-ft 10% OV-11 column. All solvents and reagents used were not purified prior to use, and melting points were uncorrected.

Nitration of 3-Methylbenzotrifluoride. At 0 °C 90% nitric acid (500 g, 7.2 mol) was stirred as 3-methylbenzotrifluoride (160 g, 1.0 mol) was added at a rate such that the reaction temperature never exceeded 5 °C. Upon complete addition the solution was stirred for 15 min, after which the reaction was poured cautiously over ice/water (2 kg). The layers were separated and the aqueous layer was washed with dichloromethane (1 × 500 mL). The organics were combined, dried ($MgSO_4$), filtered, and concentrated to 200 g of the crude nitration mixture (97%). Capillary GLC analysis showed a mixture of 42% 3-methyl-2-nitrobenzotrifluoride (**3**), 36% 3-methyl-6-nitrobenzotrifluoride (**6**), 20% 3-methyl-4-nitrobenzotrifluoride (**4**), and 2% 3-methyl-5-nitrobenzotrifluoride (**5**). Each component was compared to an authentic sample prepared via an unambiguous route.[7]

Disulfide Reduction of the Nitration Mixture. At 40 °C, $Na_2S{\cdot}9H_2O$ (84 g, 0.35 mole) was treated in 1:1 methanol/water (200 mL) with sulfur (13.8 g, 0.4 mol) in one portion followed by methanol (100 mL). Within 1 h all solids had dissolved, and ammonium chloride (4.7 g, 0.0875 mol) was added and stirred for 15 min. The temperature was brought to 75 °C in a separate reactor containing the nitration mixture (57.4 g, 0.28 mol) in 1:1 methanol/water (50 mL). The polysulfide reagent was added slowly over a 1-h period. After a brief exotherm the reaction slowed and 25% NaOH was added to maintain pH 11–12. After a total of 5 h the mixture was cooled, diluted with water (500 mL), and extracted with dichloromethane (3 × 100 mL). The organic layer was treated with gaseous HCl resulting in the precipitation of the hydrochlorides of **7**–**9**. Filtration recovered 29.5 g (88%) of the yellow anilinium salts. Concentration of the filtrate gave 24.8 g (95%) of a dark oil which crystallized on standing. Recrystallization from methanol or methylcyclohexane gave analytically pure **3**: ^1H NMR ($CDCl_3$) 2.2 (s, 3 H), 7.3 (s, 4 H); ^{19}F NMR ($CDCl_3$) +2.3; mp 32–33 °C; bp 48–49 °C at 0.1 mmHg.[7]

Reductive Deamination of 7, 8, and 9. The reduction was run as shown above with 17.7 g of the nitration mixture. The crude products, extracted into dichloromethane, were treated slowly with 50% sulfuric acid (10 mL) at 0 °C. The acid layer was estimated to have 50 mmol of anilinium hydrogen sulfate salt dissolved while the organic phase was concentrated to give 7.0 g of **3**. Thus this acidic solution was treated with the cautious addition of $NaNO_2$ (3.5 g, 52 mmol) in water (15 mL) at 0 °C. The reaction was vigorous and upon complete addition of nitrite this cold solution was added dropwise to ethanol (20 mL) and Cu–bronze (0.5 g) at reflux. The resulting solution was refluxed for 30 min, after which it was cooled, diluted with dichloromethane (100 mL) and washed with water (1 × 30 mL). The organic layer was dried ($MgSO_4$), filtered, and fractionally distilled to recover 6.6 g of **1** (83%).

Reduction of 3-Methyl-2-nitrobenzotrifluoride (3). A Parr hydrogenation apparatus was used to reduce **3** (5.2 g, 25 mmol) in ethanol (100 mL) with Raney Ni catalyst (1 g). Hydrogen was charged to 50 psi, and the apparatus was shaken for 24 h at room temperature. At the end of this period of time the catalyst was filtered and concentration of the solvent gave 4.2 g of aniline (**2**) (95%): ^1H NMR ($CDCl_3$) 2.1 (s, 3 H), 4.0 (bs, 2 H), 6.6–7.2 (m, 3 H); ^{19}F NMR ($CDCl_3$) −5.2; bp 64–66 °C at 5 mmHg.[7]

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Registry No. **1**, 401-79-6; **2**, 88301-98-8; **3**, 81-20-9; **4**, 67192-42-1; **5**, 96783-80-1; **6**, 87617-21-8; **7**, 23984-80-7; **8**, 103981-82-4; **9**, 103981-83-5.

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[7] These products were identical in all respect with those materials reported in ref 3.

Improved Synthesis of 1,4,5,8,9,12-Hexaazatriphenylene

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The synthesis and some properties of 1,4,5,8,9,12-hexaazatriphenylene (HAT, **3**) have recently been reported.[2] HAT is a stronger electron acceptor than 1,10-phenanthroline and forms mono-, di, and trichromium tetracarbonyl complexes. The previously reported synthesis is an involved 10-step procedure. Because we required multigram quantities of HAT, we needed a more practical preparation.

The approach we took is shown in Scheme I. Although 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, **1**) has been reduced to the hexaamine with boiling phenylhydrazine[3] and more recently catalytic hydrogenation,[4] we explored reduction with sodium in liquid ammonia, which has previously been used for reduction of mononitroarenes.[5,6] Symmetric peralkyl derivatives of HAT have recently been synthesized by condensation of hexammine **2** with α-diketones; the method reported was not successful in producing HAT itself.[7]

A wide variety of standard methods for reduction of aromatic nitro groups were surveyed without success. The low stability of HAB was a contributing factor in these failures. A review of the literature showed that various mononitroarenes had been successfully reduced to amines by sodium in liquid ammonia in the presence of methanol.[5,6] In these cases typically 10 equiv of alcohol were used.

When we applied these procedures to the reduction of TATB, some HAB was produced but in low and variable yield. Instead of the transient blue color expected in a dissolving metal reduction, the reaction mixture was an intense purple color. A review of the earlier literature[4] indicated that this color was typical of the reaction of nitroarenes with sodium and liquid ammonia in the absence of hydrogen donors. We therefore examined the use of very high concentrations of the hydrogen donor in these reactions.

In our case the use of 42 equiv of methanol per nitro group gave reproducible yields of HAB in excess of 90%. Little or no purple color formation occurred; the usual transient blue color followed by a fading yellow color was observed. We made no attempt to determine the minimum amount of methanol required. It seems likely that protonation of the intermediate reduction products is in competition with other reaction routes such as coupling and that use of high concentrations of the hydrogen donor favor the desired reduction to an amine.

HAT of good purity was produced in over 80% yield by simply adding freshly prepared HAB to 40% aqueous glyoxal. The crude HAT was purified to give material of analytical quality by simple column chromatography. Overall this procedure gives analytical quality HAT in

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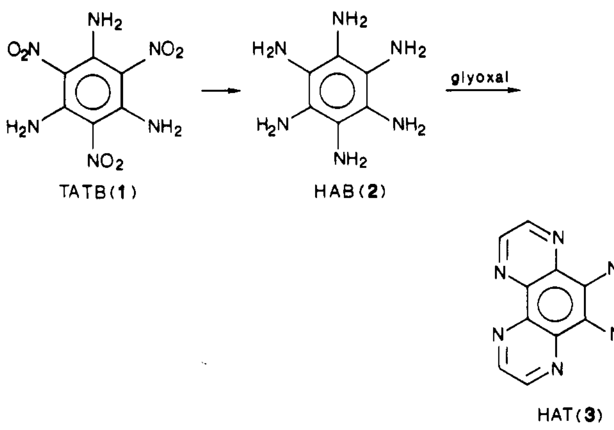
Scheme I



TATB(**1**) HAB(**2**) HAT(**3**)

better than 75% yield based on TATB.

Although the modified reduction procedure reported here has not been tested on other polynitroarenes, we believe that it would be generally useful method for the synthesis of polyaminoarenes from the corresponding polynitroarenes. It would also be of interest to examine the reduction of other types of substrates with sodium in liquid ammonia in the presence of very high hydrogen donor concentrations.

Experimental Section

Infrared spectra were taken on a Nicolet 5DXE FT-IR instrument. Microanalyses were performed by Galbraith Laboratories. TATB was purchased from Chemtronics, Inc. and used as received. All other reagents were used as received. *Caution! TATB is a military explosive. Although relatively insensitive to accidental detonation, it should be used only in small quantities with appropriate safety precautions.*

Preparation of HAB (2). A 1-L 3-neck flask equipped with mechanical stirrer, gas inlet, and gas condenser was charged with TATB (1; 7.1 g, 27.5 mmol) and methanol (137 mL, 3.39 M). Approximately 400 mL of ammonia was then condensed into the flask. Stirring was started and sodium (16 g, 696 mmol) added in small pieces at a rate sufficient to cause gentle reflux of the ammonia. After the sodium addition was complete and the blue color discharged, the gas condenser was removed and the ammonia allowed to evaporate. When the mixture reached room temperature, the solids were collected by vacuum filtration and washed with ethanol and finally diethyl ether to give 2 (4.39 g, 26.1 mmol) as a cream-colored solid in 95% yield. This material was of sufficient quality to use without purification but decomposed significantly on standing in air for 24 h. Aqueous solutions of 2 decomposed completely in 24 h. On heating in air 2 darkened at 150 °C and decomposed at 240–255 °C (lit.[3] decomposition point (in H_2) 247–248 °C). IR (KBr, cm^{-1}): 3353, 3269, 1644, 1490.

Preparation of HAT (3). Technical grade 40% aqueous glyoxal (approximately 50 mL) was cooled in an ice bath and freshly prepared HAB (4.39 g, 26.1 mmol) added in portions to the stirred solution. After the addition was complete, the solution was allowed to warm to room temperature. A copious precipitate appeared within 1 h. After stirring for 18 h, the mixture was poured into 300 mL of water, and the solids were collected by vacuum filtration. The solids were washed well with water, ethanol, and diethyl ether and then dried to give HAT (5.05 g, 21.7 mmol) in 83% yield as a tan solid. Of this 2.38 g was continuously extracted for 48 h with 500 mL of chloroform. Decolorizing carbon (0.15 g) was added to the chloroform solution, and the solution was gently boiled for 15 min. The solution was cooled to room temperature and poured onto a column of 500 g of dry alumina. A yellow band eluted in the middle of the HAT elution. Two fractions were collected. Evaporation of eluent before the yellow band gave 0.40 g of HAT as a white solid. Anal. Calcd for $C_{12}H_6N_6$: C, 61.54; H, 2.56; N, 35.90. Found: C, 61.57; H, 2.64; N, 35.56. The IR spectrum was identical with that of material prepared by previously reported methods. IR (KBr, cm^{-1}): 1968, 1469, 1377, 1328, 1223, 1096, 871. Evaporation of the remaining eluent gave 1.95 g of HAT as a white solid, with an IR spectrum identical with that of the preceding fraction. Anal. Found: C, 61.25; H, 2.66; N, 36.00.

Registry No. 1, 3058-38-6; 2, 4444-26-2; 3, 79790-37-7; glyoxal, 107-22-2.

Voltammetry in (Toluene)$_3$-Tetrabutylammonium Tetrafluoroborate, a Novel Liquid "Hydrocarbon Electrolyte"

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The electrochemical voltammetric behavior of organic substances, involving as it generally does the generation of charged intermediates, is very sensitive to the nature of the medium in which the experiments are conducted.[1-5] A variety of homogeneous and heterogeneous processes can be affected by changes in the solvent and/or supporting electrolyte. For example, many studies have shown that the electrochemical reduction of aromatic hydrocarbons is highly sensitive to the presence of proton donors in the medium.[1-3] Furthermore, since ion-pairing effects can be important in such studies, the polarity of the solvent can have a major effect upon the electrochemical behavior of substances dissolved in it. For this reason, our attention was recently attracted by the report of a novel liquid "hydrocarbon electrolyte" solvent system composed of tetrabutylammonium tetrafluoroborate and toluene in 1:3 molar ratio.[6] We were interested in the potential utility of this solvent (which we refer to herein as T3–TBATFB) for studies on the voltammetric behavior of aromatic hydrocarbons as well as intrigued by the possibility that this solvent might present a "hydrocarbon-like" microenvironment in which to carry out electrochemical experimentation. Little information was provided concerning such matters in the original publication, which was devoted to the voltammetry of an iron–sulfur cluster. We have examined the voltammetry of several aromatic substrates in this novel solvent system. Our results indicate that such voltammetry, with a few exceptions, resembles to a surprising degree that of the same substances in a typical dipolar aprotic solvent, dimethylformamide (DMF).

Cyclic voltammetry was carried out at a mercury-coated platinum electrode[7] at a scan rate of 500 mV s^{-1} and DC polarography was carried out at a conventional dropping mercury electrode. The cyclic voltammogram of perylene in T3–TBATFB, scanned from −1.20 to −2.75 V (vs. Ag/0.1 M $AgNO_3$ in acetonitrile) and back is shown in Figure 1. The most characteristic features of this voltammogram are the presence of a reversible couple at −2.00 V, an irreversible reduction peak at −2.58 V, and an oxidation peak at −1.46 V, which is not present if the initial potential scan

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