1,3,5-Tris(4-aminophenyl)benzene derivatives: design, synthesis *via* nickel-catalysed aromatic amination and electrochemical properties

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Received (in Cambridge, UK) 10th July 2002, Accepted 9th September 2002
First published as an Advance Article on the web 11th October 2002

Nickel-catalysed polycondensation reactions of 1,3,5-tris(*p*-chlorophenyl)benzene with secondary cyclic and acyclic amines afforded the corresponding triarylamines in good yields. Oxidation of these materials creates dications diradicals that are stable over several minutes at room temperature. The electronic and magnetic properties of these dications were investigated by cyclic voltammetry, chronoamperometry, UV–VIS and EPR spectroscopy.

Introduction

Aromatic rings bearing one or more amino substituents are the subject of current research interest due to their strong electron donor character and because of their ability to form stable aminium radical cations. Thus, arylamines display a wide range of potential applications in material sciences since their ease of modification allows tuning of their optical, electronic or conductive properties.[1] For this reason, they have been used in many fields such as hole-transport materials for organic electroluminescent display devices, sensors, photoreceptors, transistors or batteries.[2–12] Arylamines also constitute the source of stable aminium radical cations which can act as mild oxidising agents[13] or electrocatalysts.[14]

In this context, 1,3,5-triaminophenylenes are particularly interesting because the *meta* connection of amino radical cations favours spin alignment and allowed ferromagnetic coupling between electron spins in the organic radical.[15] However, the modest yields of copper-mediated Ullmann couplings that are conventionally used to prepare 1,3,5-triaminophenylbenzenes have limited the access to this class of material.[16]

New nickel-catalysed methods to form arylamines have recently emerged from our group. We have reported the use of catalyst combinations of *in situ* generated colloidal Ni(0) associated to 2,2′-bipyridine or *N*-heterocyclic carbenes which provided efficient routes to substituted anilines.[17] In addition to its utility in amination reactions of aryl chloride substrates, the Ni–2,2′-bipyridine catalyst has also been shown to be effective for polyamination or selective monoamination of aryl di- and trichlorides.[18]

These results suggested that efficient conditions to generate polyarylamines with *meta* regiochemistry could be found. Here, we report the use of this nickel-catalysed chemistry to form symmetrical 1,3,5-tris(aminophenyl)benzenes **2** that contain *p*-phenylene amine units connected by a *m*-phenylene unit. The examination of the electronic properties of new materials **2** revealed also an original behaviour.

Results and discussion

Synthesis

The chemical structure and the synthetic route to compounds **2** are depicted in Scheme 1. Tris(4-chlorophenyl)benzene **1** was used as a building block for the synthesis of 1,3,5-tris(4-aminophenyl)benzene **2** and was prepared in 73% yield by cyclotrimerisation of 4-chloroacetophenone with $SiCl_4$ in dry EtOH at 25 °C.[19] Reaction of **1** with secondary cyclic and acyclic amines using Ni(0) associated to 2,2′-bipyridine as ligand in THF at 65 °C for 10 hours gave 1,3,5-tris(4-aminophenyl)benzene derivatives **2** in good yields for a process that forms three new aromatic carbon–nitrogen bonds (Scheme 1). Reaction of **1** with cyclic amines was performed using 10 mol% Ni per carbon–chlorine functionality (products **2a**, **2b** and **2c**) while coupling of *N*-methylaminoacetaldehyde dimethyl acetal with **1** was run using 20 mol% Ni (product **2d**).

Recent electrochemical investigations on 1,3,5-tripyrrolidinobenzene provided conclusive proof that the dimerisation of the radical cation generated from this arylamine led to the formation of a covalent σ bond (Scheme 2).[20]

In contrast to 1,3,5-triaminobenzenes, the oxidation of compounds **2**, which are expected to be better electron-donors, has not yet been described in the literature.

The electronic properties of new materials **2** were therefore examined by several electrochemical techniques and EPR spectroscopy.

Electrochemical experiments

The electrochemical behaviour of **2a**–**d** derivatives has been studied on both glassy carbon and platinum electrodes, by cyclic voltammetry, linear scan voltammetry at rotating disk electrodes, constant potential coulometry, double step chronoamperometry and chronocoulometry. Compounds **2** display very similar behaviour, except for **2a** for which adsorption of the oxidation product(s) has been evidenced (see below). The following discussion will focus essentially on derivatives **2a** and **2d**.

DOI: 10.1039/b206689k

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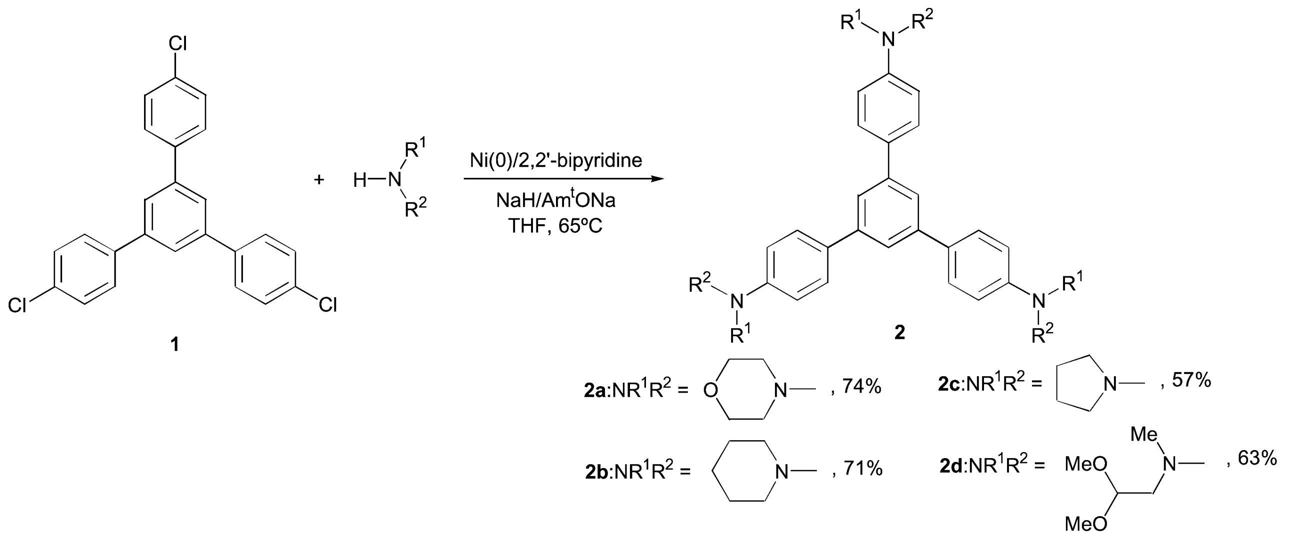
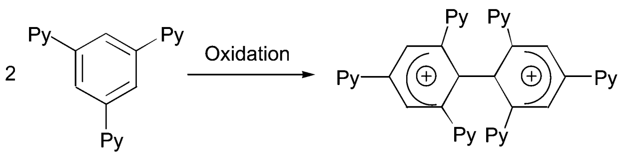


Scheme 1



Scheme 2

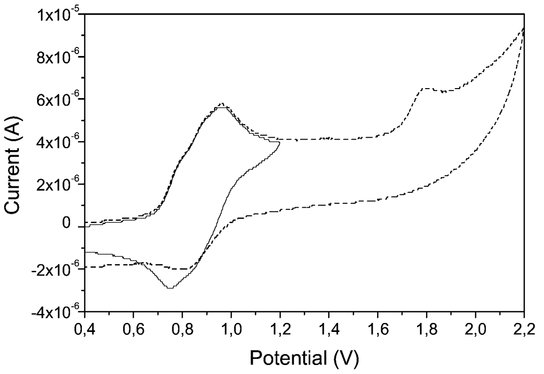


Fig. 1 Cyclic voltammogram of **2d** in CH_3CN–0.1 M Bu_4NPF_6; $v = 50$ mV s^{-1}; $T = 293$ K; $c = 10^{-3}$ M.

Typical cyclic voltammograms of **2d** obtained at a scan rate of 50 mV s^{-1} in dry acetonitrile solution are depicted in Fig. 1.

When the potential scan started from +0.4 V towards the positive direction, the first oxidation appeared near +0.80 V and was immediately followed by a second well-defined peak located at +0.96 V. The relative intensity of these anodic signals was close to unity and was independent of the scan rate (from 10 to 2000 mV s^{-1}). Both of the anodic signals are diffusion-controlled as shown by the Randles–Sevcik equation.[21]

At 50 mV s^{-1}, on scan reversal from +1.20 V, two corresponding cathodic signals were recorded: the first one at about +0.85 V, followed by a peak located at +0.75 V. Extending the potential scan up to +2.20 V in the anodic direction led to the observation of another peak located at +1.80 V, with the concomitant decrease in the intensity of cathodic signals recorded on scan reversal. The other compounds (**2a**–**c**) showed voltammetric characteristics similar to that of **2d**, with anodic peaks located between +0.9 to 1.0 V. However, distinction of the preceding anodic wave from the main peak (as well as their cathodic counterparts) was more or less pronounced depending on the nature of the substituent on the 1,3,5-tris[4-aminophenyl]benzenes. This potential window is similar to oxidation potential values that were previously reported for other tertiary aromatic amines.[22,23] Constant potential coulometry performed at +1.1 V (a potential value including both peaks) demonstrates the transfer of 2 electrons per molecule. The same experiment carried out at a potential value corresponding to the first oxidation was prevented because the two electron processes are located too close to each other, but one can reasonably ascribe the exchange of 1 electron per molecule to the first oxidation, followed by extraction of one additional electron at the well-defined peak, on the basis of the 1 : 1 ratio always observed by cyclic voltammetry for these two successive processes. Confirmation of the exchange of 2 electrons per molecule during the whole anodic reaction was given by chronoamperometry at ultramicroelectrodes (radius: 50 µm) using ferrocene as standard. All these results suggest the formation of a radical cation (first peak), which is quite easily oxidised into diradical dication species (main peak), which are stable enough to survive on the time scale of the experiment. Such stability is attractive, since radical cations arising form the electrochemical oxidation of aromatic amines are usually not very stable in solution at ambient temperature unless they are substituted in the *para*-position.[23–25] Relatively stable dications and/or trications have also been reported as oxidation products of tris(diarylamino)benzene derivatives.[15,25,26] In the present case, the enhanced stability can be attributed to possible hole-transport through the adjacent conjugated aryl groups. No dimerisation was evidenced during anodic redox switching of derivatives, as ascertained by recording the cyclic voltammograms at various sample concentrations, this is in contrast to observations during oxidation of other tertiary aromatic amines.[20,22,23,27] Absence of dimerisation could be explained by steric hindrance.

The stability of radical cations produced upon oxidation of **2a** and **2d** derivatives was next evaluated by cyclic voltammetry at various scan rates. Typical results are shown in Figs. 2 and 3, the curves are presented after using normalised currents with respect to square root of potential scan rate (constant criteria for diffusion-controlled reactions[21]). Under these conditions, the cathodic-to-anodic peak current ratio constitutes a direct measurement of the stability of species formed at the electrode surface on the forward potential scan (that is, those detectable on scan reversal). As shown, decreasing scan rate resulted in the progressive decrease in the cathodic-to-anodic current ratio, for both derivatives, which indicates a significant decay in the radical cation species when extending the time elapsing between their formation on forward scan and subsequent reduction on scan reversal. Intermediate species resulting from oxidation of **2d** were found to be more stable than for **2a**. Quantitative characterisation of their stability was achieved by double-step

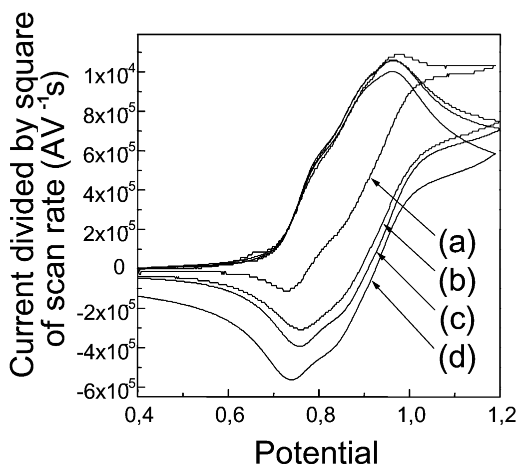


Fig. 2 Cyclic voltammogram of **2d** in CH_3CN–0.1 M Bu_4NPF_6; T = 293 K; c = 10^{-3} M; (a) 5 mV s^{-1}, (b) 10 mV s^{-1}, (c) 50 mV s^{-1}, (d) 200 mV s^{-1}.

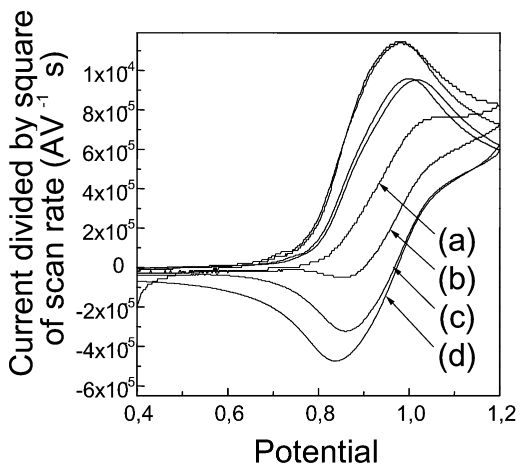


Fig. 3 Cyclic voltammogram of **2a** in CH_3CN–0.1 M Bu_4NPF_6; T = 293 K; c = 10^{-3} M; (a) 5 mV s^{-1}, (b) 10 mV s^{-1}, (c) 50 mV s^{-1}, (d) 200 mV s^{-1}.

chronoamperometry,[21] by application of the model for following reaction mechanism (EC, where E is the electron transfer corresponding to the formation of radical cations, and C is the chemical pathway responsible for their decay), for various times of potential switching in the 1–120 s. Decay of radical cations (and/or diradical dications) originating from oxidation of derivatives **2a** and **2d** was characterised by speed constants of 0.15 and 0.012 s^{-1}, respectively, in agreement with the higher stability observed for **2d** by cyclic voltammetry (Fig. 2).

These values correspond to a half-live of typically few seconds to minutes in this medium at room temperature. Large scale electrolysis performed at a potential of +1.1 V yields a blue solution that shows a broad UV–VIS absorption at about 750 nm. Even if all the **2d** can be electrolysed (as ascertained by total disappearance of its characteristic peaks when performing cyclic voltammetry at the end of the electrolysis), the quantitative production of radical cations (and/or diradical dications) was prevented by the long time required to complete the electrolysis (>1 hour). During such extended periods, significant decay of the oxidation products is observed. For example, the blue colour was always persistent when applying a potential value of +1.1 V, but weakened and turned dark green when the anodic potential was stopped, and re-appeared again after re-imposing the +1.1 V value. The radical cation decay mode remains unexplained at this stage.

As shown in Fig. 2 (relative to **2d** derivative, which exhibits the largest separation between the two successive electron transfers), the first redox couple looks fully reversible (about 60 mV separation between anodic and cathodic counterparts) while the second one appears less reversible (more than 100 mV separation). The first process agrees well with the monoelectronic formation of a radical cation followed by its reduction to give back the starting molecule.

Finally, one should mention the "special" behaviour of derivative **2a** on glassy carbon, for which oxidation led to the formation of an adsorbed film on the electrode surface. As shown in Fig. 4, the voltammetric curves recorded using rotated disk electrodes reveal a classical diffusion-controlled behaviour for derivative **2d** (curve A), while significant decrease in the "stationary currents" was rapidly observed as a consequence of progressive surface coverage of the electrode upon electrochemical oxidation of derivative **2a** (curve B).

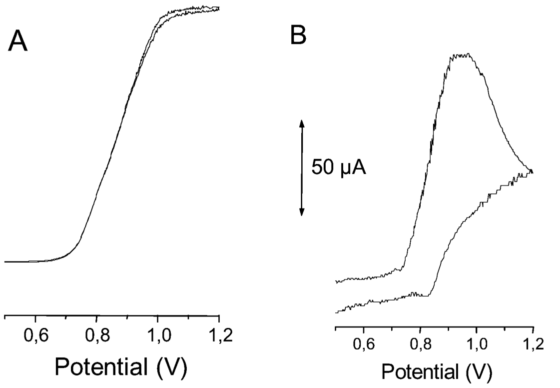


Fig. 4 Forward and reverse linear scan voltammograms of **2d** (A) and **2a** (B), obtained on rotating disk glassy carbon electrode, in CH_3CN–0.1 M Bu_4NPF_6; v = 20 mV s^{-1}; T = 293 K; c = 10^{-3} M.

On scan reversal, currents did not reach the expected "zero" value but passed to the negative range, suggesting possible reduction of the adsorbed species formed on forward scan. This behaviour was highlighted even better by increasing the scan rate (Fig. 5).

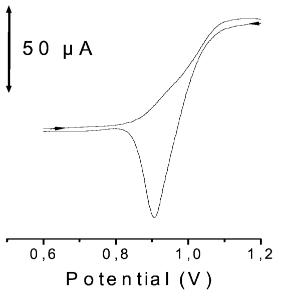


Fig. 5 Forward and reverse linear scan voltammograms of **2a**, obtained on rotating disk glassy carbon electrode, in CH_3CN–0.1 M Bu_4NPF_6; v = 250 mV s^{-1}; T = 293 K; c = 5.10^{-4} M.

This adsorption behaviour prevents extensive electrolysis as well as quantitative coulometry measurements. Chronocoulometric experiments carried out on this product have demonstrated an adsorption of the oxidised product as a monolayer on the electrode surface.

EPR experiments

The neutral compounds **2** were colorless in $CHCl_3$ solution. Chemical oxidation of **2a**, selected as representative for this study, by 1 molar equiv. of $SbCl_5$ in $CHCl_3$ at ambient temperature was accomplished immediately and yielded a colloidal blue solution which showed a single broad-line EPR spectrum with a spectral width of ~ 40 Gauss as shown in Fig. 6A. Proton hyperfine couplings broadened the spectrum so that clear resolution of the ^{14}N line pattern was not observed.

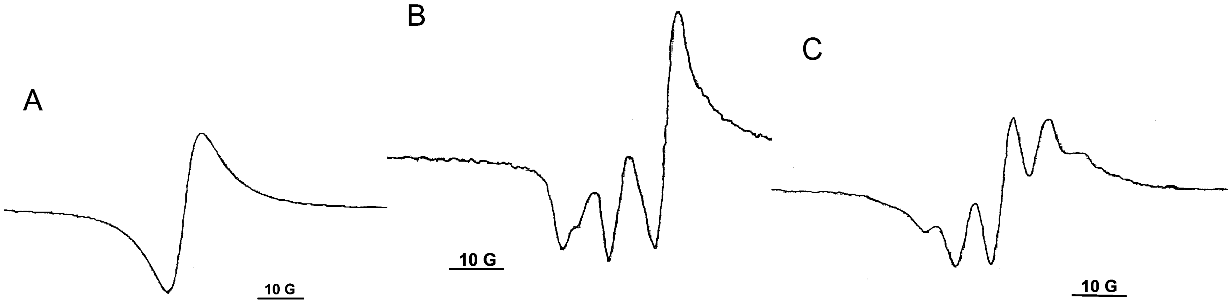


Fig. 6 EPR spectra of **2a** after oxidation with 1 equiv. (A) $SbCl_5$ (B) $THClO_4$ (C) PIFA in $CHCl_3$ at 293 K. The EPR instrument settings were as follows: 10 mW; modulation amplitude, 4 Gauss.

When 1 equiv. thianthrenium perchlorate ($TH^+ClO_4^-$)[28] is added to a solution of **2a** in $CHCl_3$, the EPR spectrum at room temperature is a combination of the broaden spectrum previously observed with $SbCl_5$ and a quintet (Fig. 6B).

Treatment of **2a** in $CHCl_3$ with bis(trifluoroacetoxy)iodobenzene (PIFA),[29] a milder oxidant than $THClO_4$ and $SbCl_5$, yielded after a few minutes, a blue solution which rapidly turned deep red. The radical cation generated from **2a** by this method is relatively stable at room temperature displaying a qualitative half-life of 0.25 h. The fluid solution gives the well resolved quintet EPR spectrum depicted in Fig. 6C. The hyperfine structure consists of five lines having a splitting constant of 8.6 Gauss. The observed quintet spectrum is typical for cation radicals where an unpaired electron is equally coupled to two nitrogen atoms. This hyperfine structure was however unexpected for the radical cation generated from **2a** and cannot be due to the interaction of the hole with two nitrogen nuclei of the same molecule. The splitting constant was also significantly higher than the value generally reported for arylamine cations radicals (5–6 Gauss).[30]

It has been demonstrated that the radical cation formed during the first step of triaminobenzene oxidation can form charge-transfer complexes with excess educt.[31] With compound **2a**, we have however carried out the oxidation with stoichiometric amounts of PIFA and the presence of unreacted **2a** was not detected in the reaction medium. A different reaction pattern might therefore be proposed for this substrate.

We suppose that, after the formation of the first radical cation, $\mathbf{2a}^{\bullet+}$ spontaneously reacts to give, by a charge-transfer process, a bimolecular diradical dication $[\mathbf{2a}^{\bullet}\mathbf{2a}^{\bullet}]^{2+}$ in which the aromatic rings lie above each other in parallel planes and where the hole is localised to an extent on two nitrogen nuclei (Fig. 7).

The ability of **2a** to form charge transfer complexes was further demonstrated by reacting this compound with tetracyanoethylene, a strong electron acceptor. Addition of 1 equiv. tetracyanoethylene into a $CHCl_3$ solution of **2a** yielded immediately a green solution showing a single EPR signal without any hyperfine structures (Fig. 8).

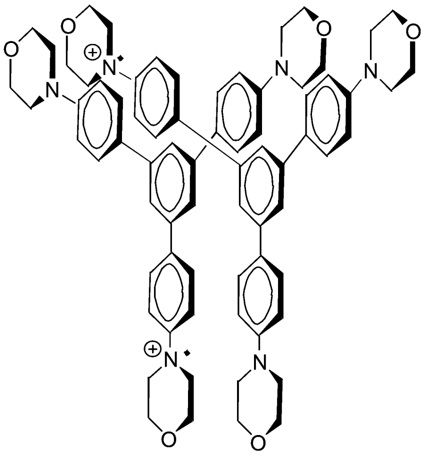


Fig. 7 An assumed structure for the π-dimer of $\mathbf{2a}^{\bullet+}$.

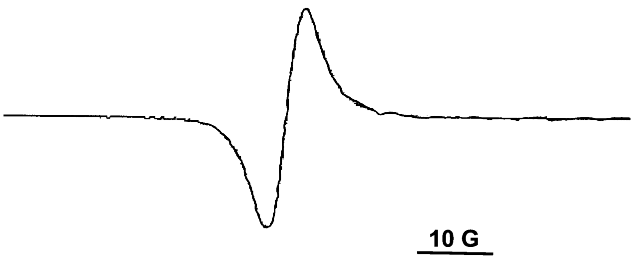
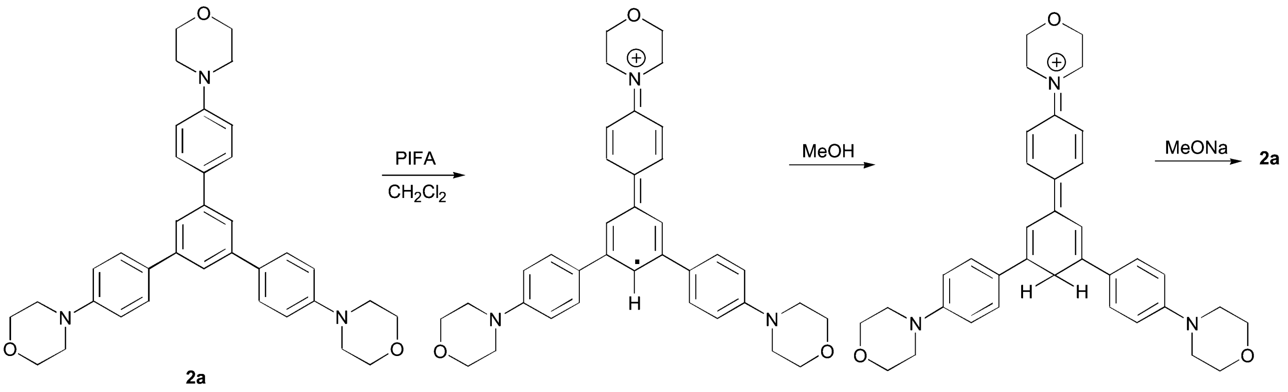


Fig. 8 EPR spectrum of the **2a**–tetracyanoethylene complex in $CHCl_3$ at 293 K. The EPR instrument settings were as follows: 10 mW; modulation amplitude, 4 Gauss.

To provide further evidence for π-dimerisation, we carried out chemical oxidation of compound **2a** with PIFA, in the dark, under a nitrogen atmosphere according to the report of Effenberger *et al.* describing the synthesis of dimeric σ-complexes.[32] The oxidant (1 equiv.) in CH_2Cl_2 was added, within 10 s, to a solution of **2a** in CH_2Cl_2. After 10 min of stirring, the reaction mixture was evaporated to dryness. One equivalent of MeONa in MeOH was then added and the composition of the crude reaction mixture was determined by NMR. Under the given experimental conditions, the ^1H and ^{13}C NMR spectra revealed the complete absence of a benzidine moiety and only the starting material **2a** was recovered in a nearly quantitative yield. These results argued strongly for the π-dimeric nature of the materials obtained after oxidation. It is likely that the only reaction pathway possible for the radical $\mathbf{2a}^{\bullet+}$ formed during the first step is hydrogen abstraction from MeOH followed by rearomatisation by deprotonation by MeONa (Scheme 3). The contrasting behaviour of compounds **2** compared to 1,3,5-triaminobenzenes can be explained by the higher steric hindrance of the aromatic core which impeded the formation of σ-dimers.

Conclusion

In summary, the high yield synthesis of arylamines by nickel-catalysed chemistry can be used to produce new 1,3,5-tris-[4-aminophenyl]benzene derivatives **2**. These materials were studied by cyclic voltammetry and EPR spectroscopy and showed a number of interesting features. Oxidation of neutral precursors **2** can generate mono- $\mathbf{2}^{\bullet+}$ or di(cation radical)s $\mathbf{2}^{2\bullet 2+}$. Compared to 1,3,5-triaminobenzenes, compounds **2** are easier to oxidise and yield cations of higher stability. No σ-dimerisation of the intermediate radical cation $\mathbf{2}^{\bullet+}$ was observed and EPR studies suggest a π-dimerisation. From the synthetic and



Scheme 3

electrochemical studies reported here, it is clear that nickel-catalysed aryl amination reactions present a significant new route to (poly)arylamines that will prove to have interesting electronic and magnetic properties.

Experimental

Materials

All experiments were carried out under a nitrogen atmosphere. THF was distilled from benzophenone–sodium adduct and stored over sodium wire. *tert*-Amyl alcohol was distilled from sodium. Crushed $Ni(OAc)_2 \cdot 4H_2O$ (Fluka) was dried under vacuum (20 mmHg) at 110 °C for 12 hours. Sodium hydride (65% in mineral oil, Fluka) was used after two washings with THF under nitrogen. 2,2′-Bipyridine was recrystallised in hexane before use. All reagents were purchased from commercial sources and were used without purification. Melting points were taken on a Tottoli apparatus and are uncorrected. Flash chromatography was performed using Kieselgel 60 (230–400 mesh, Merck). NMR spectra were recorded with Bruker AM 400 (^1H at 400 MHz, ^{13}C at 100 MHz). Chemical shifts are expressed in δ (ppm) values with tetramethylsilane (TMS) as internal reference. Yields refer to isolated yields of compounds estimated to be up to 95% pure as determined by ^1H NMR. Combustion analyses were performed by the Service central d'analyses du CNRS (Vernaison, France).

Compound **1** was prepared analogously to Smith *et al.*[19]

Syntheses

General procedure for the amination of 1,3,5-tris[4-chlorophenyl]benzene 1 using secondary cyclic amines. A 50 mL Schlenk tube was loaded with degreased NaH (1.00 g, 42 mmol), $Ni(OAc)_2$ (0.53 g, 3 mmol), 2,2′-bipyridine (1.40 g, 9 mmol), the secondary cyclic amine (60 mmol) and 15 mL THF and the mixture was heated to reflux. A solution of Am^tOH (0.53 g, 6 mmol) in 5 mL THF was then added dropwise and the mixture was further stirred for 1 h. A solution of 1,3,5-tris[4-chlorophenyl]benzene **1** (4.09 g, 10 mmol) and styrene (0.312 g, 3 mmol) in 10 mL THF was then added and the reaction was monitored by TLC. After complete consumption of the starting aryl trichloride, the mixture was cooled to room temperature, adsorbed onto silica gel and evaporated. The crude reaction mixture was purified by silica gel chromatography.

1,3,5-Tris[4-morpholinophenyl]benzene (2a). Synthesised from **1** according to the general procedure. The yield of **2a** was 74%. After chromatography on SiO_2 column, eluent EtOAc–hexanes (80 : 20), a pale yellow solid was obtained. Mp 226 °C. ^1H NMR ($CDCl_3$) δ 7.65 (s, 3H), 7.61 (d, 6H, J = 8.8 Hz), 7.00 (d, 6H, J = 8.8 Hz), 3.90–3.88 (m, 12H). ^{13}C NMR ($CDCl_3$) δ 150.6, 141.8, 132.8, 128.0, 123.4, 108.7, 60.4, 49.2. Anal. Calcd. for $C_{36}H_{39}N_3O_3$: C, 76.98; H, 7.00; N, 7.48; O, 8.54. Found: C, 76.6; H, 7.1; N, 7.4%.

1,3,5-Tris[4-piperidinophenyl]benzene (2b). Synthesised from **1** according to the general procedure. The yield of **2b** was 71%. After chromatography on SiO_2 column, eluent EtOAc–hexanes (50 : 50), a white solid was obtained. Mp 163 °C. ^1H NMR ($CDCl_3$) δ 7.61 (d, 6H, J = 8.4 Hz), 7.57 (s, 3H), 7.02 (d, 6H, J = 8.4 Hz), 3.24–3.22 (m, 12H), 1.75–1.71 (m, 12H), 1.62–1.59 (m, 6H). ^{13}C NMR ($CDCl_3$) δ 151.9, 142.1, 134.5, 127.8, 123.6, 116.4, 50.4, 25.8, 24.3. Anal. Calcd. for $C_{39}H_{45}N_3$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.1; H, 8.0; N, 7.9%.

1,3,5-Tris[4-pyrrolidinylphenyl]benzene (2c). Synthesised from **1** according to the general procedure. The yield of **2c** was 57%. After chromatography on SiO_2 column, eluent EtOAc–hexanes (50 : 50), a white solid was obtained. Mp 218 °C. ^1H NMR ($CDCl_3$) δ 7.61 (s, 3H), 7.59 (d, 6H, J = 8.4 Hz), 6.66 (d, 6H, J = 8.4 Hz), 3.35–3.33 (m, 12H), 2.05–2.03 (m, 12H). ^{13}C NMR ($CDCl_3$) δ 147.3, 145.9, 142.2, 128.0, 122.2, 111.9, 47.7, 25.4. Anal. Calcd. for $C_{36}H_{39}N_3$: C, 84.17; H, 7.65; N, 8.18; O, 8.54. Found: C, 84.2; H, 7.6; N, 8.2%.

1,3,5-Tris{4-[*N*-(2,2-dimethoxyethyl)-*N*-methylamino]-phenyl}benzene (2d). *N*-(2,2-Dimethoxyethyl)-*N*-methylamine (7.14 g, 60 mmol), **1** (4.09 g, 10 mmol), Am^tOH (1.05 g, 12 mmol), NaH (1.15 g, 48 mmol), $Ni(OAc)_2$ (1.07 g, 6 mmol), 2,2′-bipyridine (1.872 g, 12 mmol) and styrene (0.31 g, 3 mmol) were used for the synthesis of **2d** using the general procedure described above. The yield of **2d** was 63%. After chromatography on SiO_2 column, eluent EtOAc–MeOH (95 : 5), a colourless oil was obtained. ^1H NMR ($CDCl_3$) δ 7.62 (s, 3H), 7.60 (d, 6H, J = 8.5 Hz), 6.83 (d, 6H, J = 8.5 Hz), 4.56 (t, 3H, J = 5.0 Hz), 3.50 (d, 6H, J = 5.0 Hz), 3.44 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 148.6, 141.9, 128.0, 122.4, 112.1, 103.3, 55.3, 54.6, 39.3. Anal. Calcd. for $C_{39}H_{51}N_3O_6$: C, 71.21; H, 7.81; N, 6.39; O, 14.59. Found: C, 71.0; H, 7.6; N, 6.6%.

Electrochemical experiments

Acetonitrile was distilled from $CaCl_2$ under an inert atmosphere. The supporting electrolyte tetrabutylammonium hexafluorophosphate (purris. electrochemical grade, Aldrich) was used without further purification.

All electrochemical measurements were carried out using an EG&G PAR (Princeton Applied Research) model potentiostat/Galvanostat. A three electrodes system was used. Planar working platinum and glassy carbon disks Metrohm 628–10 (diameter: 3 mm) were used as working electrodes. Their surface was mechanically polished on alumina (0.05 µm) before each measurement. All the potential values cited were measured with respect to the saturated Calomel reference electrode. The auxiliary electrode was a platinum wire. Controlled potential coulometric measurements were performed using a large platinum sheet as working electrode (about 2 cm^2).

All measurements have been carried out at room temperature.

EPR experiments

EPR spectra were recorded at 25 °C using a computer-controlled Bruker ER 200 D spectrometer operating at the X band with 100 kHz modulation frequency. The following conditions were used: 10 mW; modulation amplitude, 4 Gauss; receiver gain, from 1.25×10^3 to 25×10^3.

Acknowledgements

The authors wish to thank Pr. A. Merlin and Miss S. Yagi for assistance in performing the EPR measurements.

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