Disjoint and coextensive amminium radical cations: a general problem in making amminium radical cation based high-spin polymers

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Abstract—A two-electron oxidation of N,N,N',N'-tetrakis(2-methoxyphenyl)-1,3-diaminobenzene **12** gives the diradical dication **12$^{2\bullet+}$**, which is an aza analogue of the Schlenk hydrocarbon and, like the Schlenk hydrocarbon, has a triplet ground state. However, an attempt to produce pentuplet tetraradical tetracations by extending the same ferromagnetic spin-coupling motif in a linear or a cyclic fashion was unsuccessful. Two-electron oxidations to give disjoint diradical dications (in which the charges and spins are spatially separated) are relatively easy but it proved impossible to remove the third and fourth electrons. This would require generation of coextensive radical ions in which the charges and spin distributions overlap. The results obtained with these model oligomers illustrate what is a general problem in the creation of high-spin polymers in which the spin-bearing centres are amminium radical cations. Strong ferromagnetic spin-coupling depends on the formation of coextensive rather than disjoint radical cations but the formation of coextensive radical cations with strong ferromagnetic coupling involves a large additional coulombic penalty.
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1. Introduction

Most attempts to make high-spin polymers[1–5] have used the trityl radical[1,2,6] or the isoelectronic triphenylamminium radical cation[4,5,7–13] as the spin-carrier and ferromagnetic coupling, which is 1,3-through benzene (**1a**, **1b**), 3,4′-through biphenyl (**2a**, **2b**) or 4,4″-through metaterphenyl (**3a**, **3b**) (Fig. 1). Each of these three ferromagnetic spin-coupling motifs[14] is based on that of a triplet ground state quinodimethane (**1c–3c**).[15] π-Biradicals can be classified as either disjoint (having spin distributions that are spatially separated) or coextensive (having spin distributions that overlap in space). Hund's rule only applies to coextensive systems[1,4] and all of the biradicals **1–3** are of the coextensive type. In such systems it is the extent to which the spin distributions overlap in space that determines the strength of the exchange interaction.[1,13,16] Hence, in passing along the series **1→2→3** this overlap falls off quite sharply and so does the strength of the exchange interaction. As a result the singlet/triplet splitting in **1**[15] is much larger than that in **3**.[13] This creates a problem when exploiting amminium ion based species. In these, the charge and spin distributions

roughly parallel each other. As a result hole/hole repulsion in **1b** is also much larger than hole/hole repulsion in **3b** and it is much harder to form **1b** by a two-electron oxidation of **1d** than to form **3b** by a two-electron oxidation of **3d**.[17] Hence it is fundamentally difficult to get both strong exchange interaction and easy formation of the amminium radical cation. Another problem which is similar in nature, and which is the main theme of this paper, is illustrated in Figure 2. Taking the example of the amminium radical cation based polymer **5$^{x\bullet+}$**, which would be formed by (oxidative) p-doping of the corresponding arylamine **4**, the sequence of oxidation steps is determined by electrostatics. Removal of electrons from alternate sites, to give a polymer such as **5$^{n\bullet+}$**, should be relatively easy. In this there is no overlap of the spin (and hole) distributions and **5$^{n\bullet+}$** would be of low spin. Such systems where there is no overlap (or essentially no overlap) in the spin distributions are said to be disjoint. To create a coextensive high-spin polymer such as **5$^{2n\bullet+}$** there is clearly an additional coulombic 'penalty'. Not only are the charged centres close together but the charge distributions actually overlap. In this paper the extent of this problem is explored using a series of model '1,3-through benzene' oligomers **12–14**. We show that this coulombic 'penalty' is quite severe and, that although it is easy enough to get the low spin disjoint systems, oxidation to the coextensive high-spin systems is very difficult indeed.
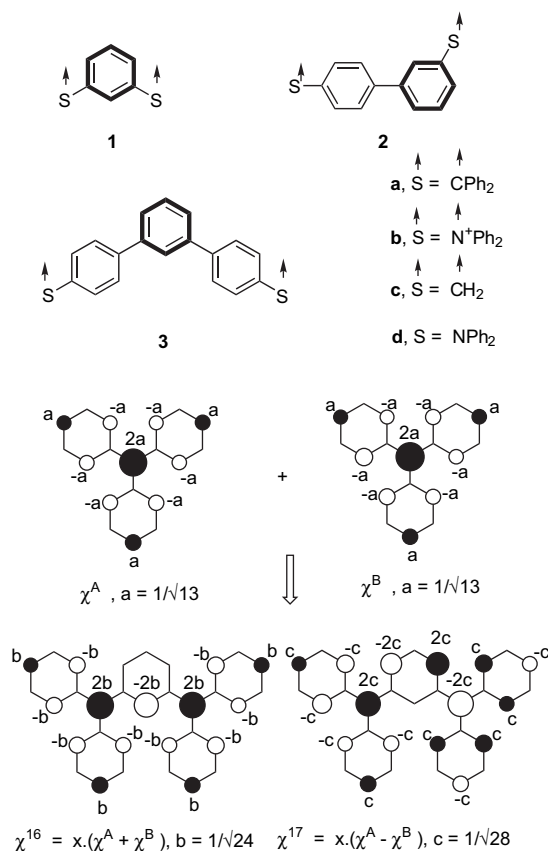
Figure 1. Top: the simplest 'building blocks' **1**–**3** that are used for the construction of high-spin polymers. In formulae **1**–**3** the ring in which the spin distributions overlap (are coextensive) is shown in bold. Bottom: formal derivation of the degenerate Huckel NBMOs of the Schlenk hydrocarbon **1a** from the NBMOs of two trityl radicals. The application of Hund's rule requires that the singly occupied orbitals are degenerate, orthogonal and coextensive. In high-spin atom-based centres (carbenes, transition metal centres, etc.) all three of these requirements are always met. In molecular systems even when the orbitals are degenerate and orthogonal they are not always coextensive. In non-coextensive (disjoint) molecular systems 'Hund's' rule no longer applies.

Figure 2. A hypothetical linear high-spin polymer $\mathbf{5}^{2n\bullet+}$ based on the repeat unit **1b** illustrating the problem associated with the formation of coextensive spins. As in all such polymers and oligomers, the amminium ion centres are generated by p-doping (oxidative doping) of the corresponding polyaryl-amine. Note that each spin is only coextensive with its nearest neighbour, otherwise they are disjoint. Only the coextensive spin distributions give ferromagnetic coupling but formation of coextensive spin distributions incurs an additional coulombic penalty.

2. Results

2.1. Synthesis

The synthesis of the oligomers is shown in Scheme 1. As well as the diamine **12**, which is the precursor to the triplet diradical dication $\mathbf{12}^{2\bullet+}$, we have made both linear **13**[7,8] and cyclic **14**[2,18] tetraamines, which should act as precursors to pentuplet tetraradical tetracations. Other than for the synthesis of the monoamine **11**,[19] palladium catalysed reactions were used for the key aryl ring–nitrogen bond forming steps.[20]

2.2. One-electron oxidation of the monoamine 11

The rate of dimerisation of the radical cation $\mathbf{11}^{\bullet+}$ is known[21] and it is known to give hexamethoxybenzidine.[21–25] Hence we were able to chose conditions for the conversion of **11** to its radical cation $\mathbf{11}^{\bullet+}$ in solutions that were sufficiently dilute for dimerisation to be very slow. The deconvoluted cyclic voltammogram of the amine **11** (Fig. 3a)[26] shows one-electron oxidation and reduction steps, which are well matched in amplitude confirming that there is a chemically
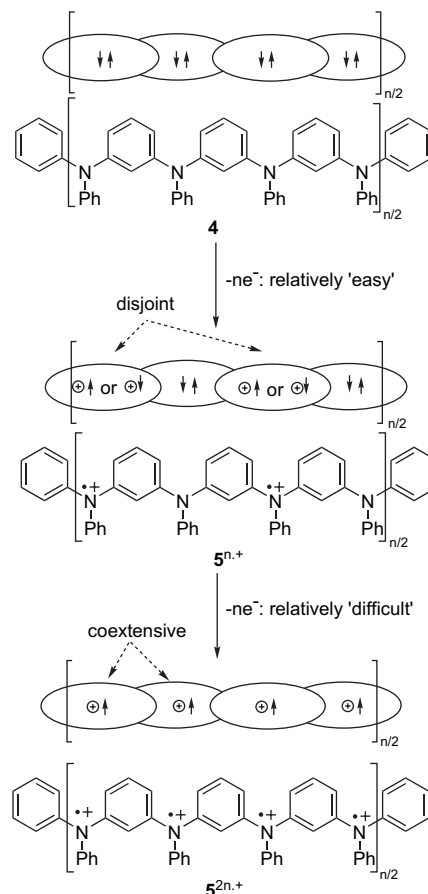
reversible one-electron transfer. Similarly, UV/visible/near IR spectroscopic studies of the oxidation in dichloromethane using thianthrenium tetrafluoroborate (THBF$_4$)[27] as the oxidant showed that there is a clean one-electron oxidation and clear isosbestic points (Fig. 4). The 4.07 eV band of the amine decreases reaching a limit exactly upon addition of 1 equiv of the oxidant. Addition of more than 1 mol of oxidant produces no change in the spectrum other than a buildup of bands due to the oxidant itself. The spectrum obtained for the radical cation $\mathbf{11}^{\bullet+}$ is very similar to that of the radical cation of tris(4-methoxyphenyl)amine and the D_0–D_1 transition is split (1.35 and 1.50 eV).[28] The oxidised solution is blue-green. EPR spectroscopic studies also confirmed that there is clean formation of the radical cation and that this is stable in solution for many hours. The spectrum of the radical cation $\mathbf{11}^{\bullet+}$ in dichloromethane at room temperature shows a 1:1:1 triplet centred at 3351G (a (^{14}N) 8.1G).[29]

2.3. One-electron and two-electron oxidation of the diamine 12

The geometry of the diamine **12** shown in Figure 5 was derived from a single crystal X-ray diffraction study. As
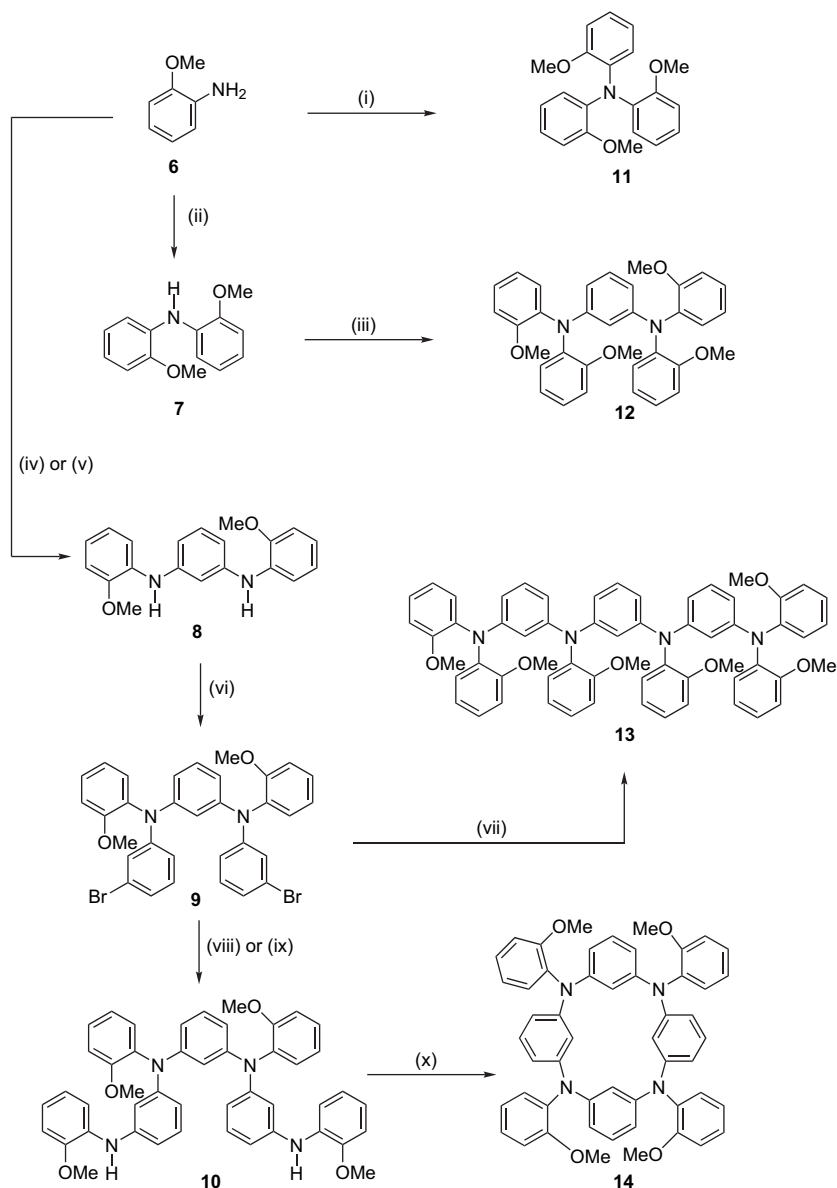
Scheme 1. Synthesis of the amines **11**–**14**. Reagents and conditions: (i) 2-iodomethoxybenzene/Cu/Na$_2$CO$_3$/*ortho*-dichlorobenzene/48 h/180 °C/40%; (ii) 2-iodomethoxybenzene/Pd(OAc)$_2$/P^{t}Bu$_3$/^{t}BuONa/toluene/12 h/100 °C/85%; (iii) 1,3-dibromobenzene/Pd(OAc)$_2$/DPPF/^{t}BuONa/toluene/36 h/100 °C/78%; (iv) 3 equiv 1,3-dibromobenzene/Pd(OAc)$_2$/P^{t}Bu$_3$/^{t}BuONa/toluene/12 h/100 °C/52%; (v) 3 equiv 1,3-dibromobenzene/Pd(OAc)$_2$/DPPF/^{t}BuONa/toluene/24 h/100 °C/80%; (vi) large excess of 1,3-dibromobenzene/Pd(OAc)$_2$/DPPF/^{t}BuONa/toluene/24 h/100 °C/70%; (vii) compound **8**/Pd(OAc)$_2$/P^{t}Bu$_3$/^{t}BuONa/toluene/18 h/100 °C/83%; (viii) 3 equiv 2-aminomethoxybenzene/Pd(OAc)$_2$/P^{t}Bu$_3$/^{t}BuONa/toluene/24 h/100 °C/90%; (ix) 3 equiv 2-aminomethoxybenzene/Pd(OAc)$_2$/DPPF/^{t}BuONa/toluene/24 h/100 °C; (x) 1 equiv 1,3-dibromobenzene/Pd(OAc)$_2$/P^{t}Bu$_3$/^{t}BuONa/dilute solution in toluene/10 days/25 °C/55%.

expected, the nitrogens are almost planar and there is a propeller-like arrangement of the surrounding phenyl rings.[9,30] Whereas a one-electron oxidation of **11** gives a trimethoxylated triphenylamine radical cation, the electrophore of **12** is effectively a dimethoxylated triphenylene. As a result, the oxidation potential of **12** is higher than that of **11** (Table 1), the radical cation **12**$^{•+}$ is less stable and it dimerises more rapidly.[23] We found that, using concentrations similar to those for the monoamine **11**, dimerisation was a significant factor, particularly for the CV studies since these required the most concentrated solutions. As shown by the unmatched areas for the CV peaks in the forward and reverse sweeps (Fig. 3b), oxidation is not chemically reversible. Furthermore, after the first anodic sweep, subsequent sweeps reveal new peaks at 0.48 V and 1.03 V, which can be assigned to the

first and second oxidations of the dimer (benzidine), respectively.[21–25] These grow in size with repeated sweeps. The first oxidation step leading from the monoradical monocation **12**$^{•+}$ is at 0.73 V (vs silver/silver chloride) but the second leading to the diradical dication **12**$^{2•+}$ is >1.3 V. This is unexpectedly high since for *N,N,N′,N′,N″,N″*-hexakis(4-methoxyphenyl)-1,3,5-triaminobenzene the first oxidation potential is at 0.67 V and the second at 0.87 V (−78 °C, CH$_2$Cl$_2$, tetrabutylammonium tetrafluoroborate, vs SCE).[31] For *N,N′*-bis[4-(diphenylaminophenyl)]-*N,N′*-diphenyl-1,3-diaminobenzene the first oxidation potential is at 0.54 V and the second at 0.68 V (CH$_2$Cl$_2$, tetrabutylammonium tetrafluorophosphate, vs SCE).[29] For *N,N′,N″*-tris[4-(diphenylaminophenyl)]-*N,N′,N″*-triphenyl-1,3,5-triaminobenzene the first oxidation potential is at 0.59 V and the second at
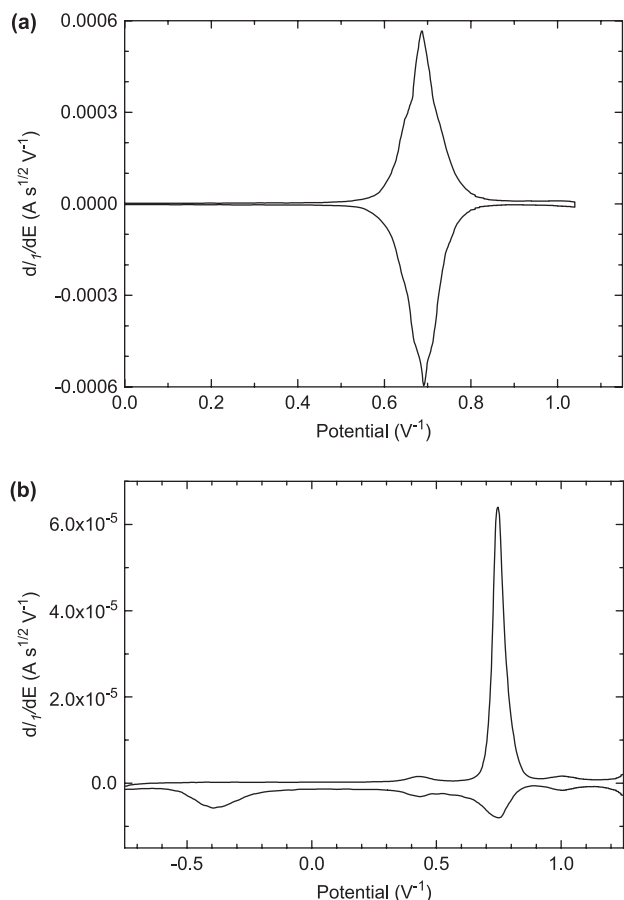
(a)

(b)

Figure 3. Cyclic voltammograms in dichloromethane with 0.1 M TBAHFP as supporting electrolyte relative to Ag/AgCl. Sweep rate of 500 mV s^{-1}. (a) Deconvoluted dI_1/dE voltammogram for 1 mM solution of monoamine **11**. (b) Deconvoluted cyclic voltammogram for 1 mM solution of diamine **12** after several cycles. The peaks at −0.42 V, 0.48 V and 1.03 V associated with benzidine formation are initially very weak but build up over time.

0.72 V (CH$_2$Cl$_2$, tetrabutylammonium tetrafluorophosphate, vs SCE)[32] and for *N,N′,N″*-tris[4-(di-*para*-anisylamino-phenyl)]-*N,N′,N″*-tri-*para*-anisyl-1,3,5-triaminobenzene the first oxidation potential is at 0.41 V and the second at 0.54 V (CH$_2$Cl$_2$, tetrabutylammonium tetrafluorophosphate,
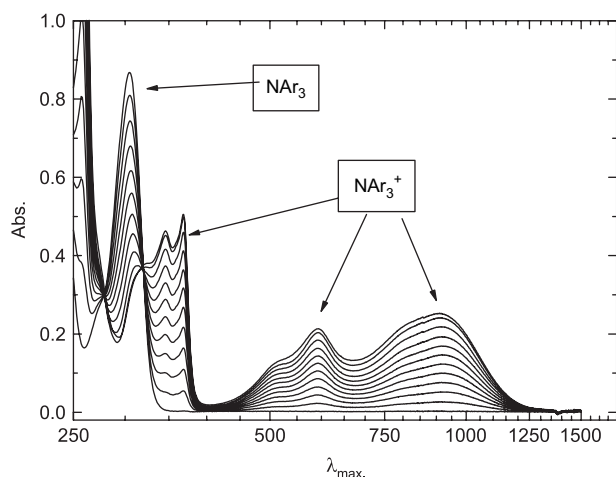

Figure 4. UV/visible/near IR spectra for the oxidation of the monoamine **11** to the radical cation **11**$^{•+}$ using THBF$_4$ in dichloromethane as the oxidant at room temperature.
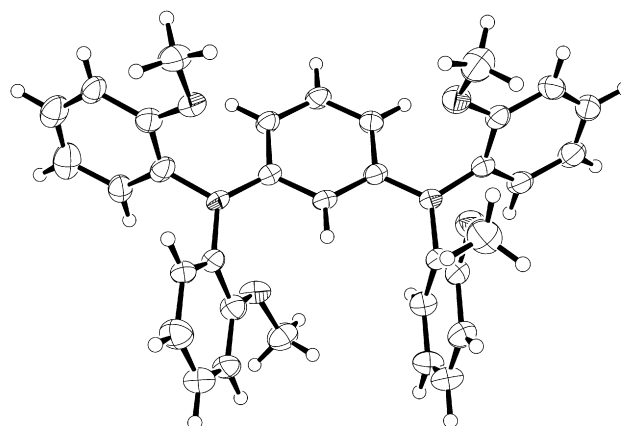
Figure 5. Geometry of *N,N,N′,N′*-tetrakis(2-methoxyphenyl)benzene-1,3-diamine **12** obtained from the single crystal X-ray structure determination. Ellipsoid probability is 50%.

vs SCE).[32] That is in **12** the separation between first and second oxidation potentials is >0.57 V whereas in closely related compounds it is <0.2 V. Tentatively, we ascribe the exceptional difficulty of removing a second electron from **12**$^{2•+}$ to a steric effect specific to the *ortho* methoxy substituents. In dichloromethane these amminium ions are contact ion paired rather than being present as free ions or solvent separated ion pairs[17] and, as in other trityl systems,[33] the counterion in the contact ion pair would most stably bridge the central nitrogen and one of the *ortho* carbons. This may not be possible in the *ortho*-methoxylated systems. As can be seen from Figure 5, the methoxy groups partly 'cover' the nitrogen. They will inhibit the approach of the counterion and this steric hindrance to ion pairing would significantly reduce the ability of the anion to shield out cation–cation repulsion. The EPR studies of the monocation **12**$^{•+}$ show that, at the lower concentration used, dimerisation is slower but still significant. The initial spectrum shows a 1:1:1 triplet centred at 3352G (a (^{14}N) 8.1G).[29] However, after 30 min at room temperature a 1:2:3:2:1 quintet centred at 3352G, (a2× (^{14}N) 5.9G) develops, which is assigned to the mono-radical of the benzidine.[34] The dimerisation is associated with a characteristic colour change from blue-green to deep green. The concentration used for the UV/visible/near IR spectroscopic studies was <10^{-2} times than that used in the CV studies (<10^{-1} times than that used in the

Table 1. Summary of CV data for the model compounds **11–14** in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte

Amine	Potential (V)			
	E_1^0	E_2^0	E_3^0	E_4^0
11	0.69[a]		—	
12	0.73[b]	>1.3	—	
13	0.73[c]	0.87	1.12	>1.3
14	0.79[a]	0.97[d]	>1.3	>1.3

Half-wave potentials E^0 are corrected to the ferrocene/ferrocenium couple, which is assumed to be +0.50 V under these conditions.
[a] Width at half height 70 mV.
[b] Width at half height 45 mV.
[c] Width at half height 50 mV.
[d] Width at half height 110 mV. Only the E_1^0 peak for the monoamine **11** shows full chemical reversibility.

EPR studies) and so dimerisation should be 10^4–10^5 times (10^2–10^3 times) slower. Essentially dimerisation is not a problem. As shown in Figure 6, when the diamine **12** is reacted with 1 equiv THBF$_4$ in dichloromethane the absorption band at 4.16 eV decreases by about half of the expected maximum amount (compare Figs. 6 and 4) when 1 mol of oxidant is added. The clear isosbestic points indicate a clean oxidation to the monoradical monocation **12$^{•+}$**. Since the thianthrene/thianthrenium couple has a redox potential of 1.1–1.3 V[35] it is only useful for electron removal up to this limit. As a result, on adding a second molar equivalent of oxidant, **12$^{2•+}$** is not formed and the only change observed is due to the buildup of THBF$_4$. To make the dication diradical of **12**, a stronger oxidant than THBF$_4$, NOBF$_4$ had to be used and, to minimise dimerisation, very dilute solutions and low temperatures. Hence, when a 10^{-3} M solution of **12** is treated with an excess of NOBF$_4$ at 0 °C, followed by rapid removal of the solvent (also at low temperatures) the solution retains the characteristic blue-green colouration of the simple amminium ion chromophore and the diradical dication **12$^{2•+}$** is obtained. This is stable in the solid state. Magnetometry shows that χT is temperature independent in the range 5–250 K although, below 5 K, χT increases and there is a slight upturn in the $1/\chi$ versus temperature plot, this is

(a) *First Equivalent*
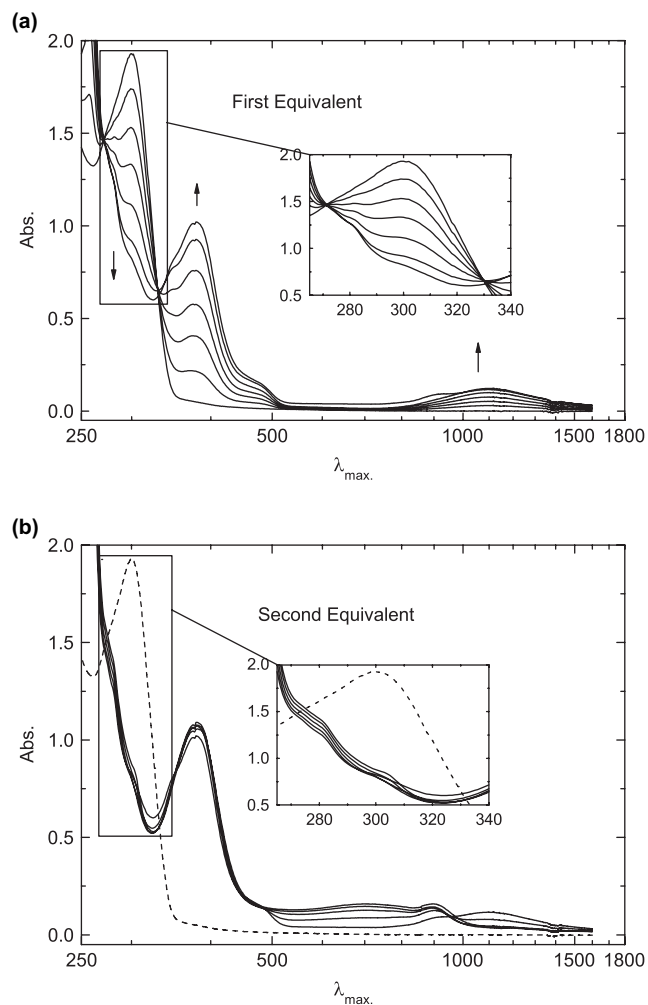
(b) *Second Equivalent*

Figure 6. UV/visible/near IR spectra for the oxidation of the diamine **12** using (a) one molar equivalent and (b) a second molar equivalent of THBF$_4$ in dichloromethane at room temperature. In (b) the dotted line shows the spectrum of the unoxidised diamine.
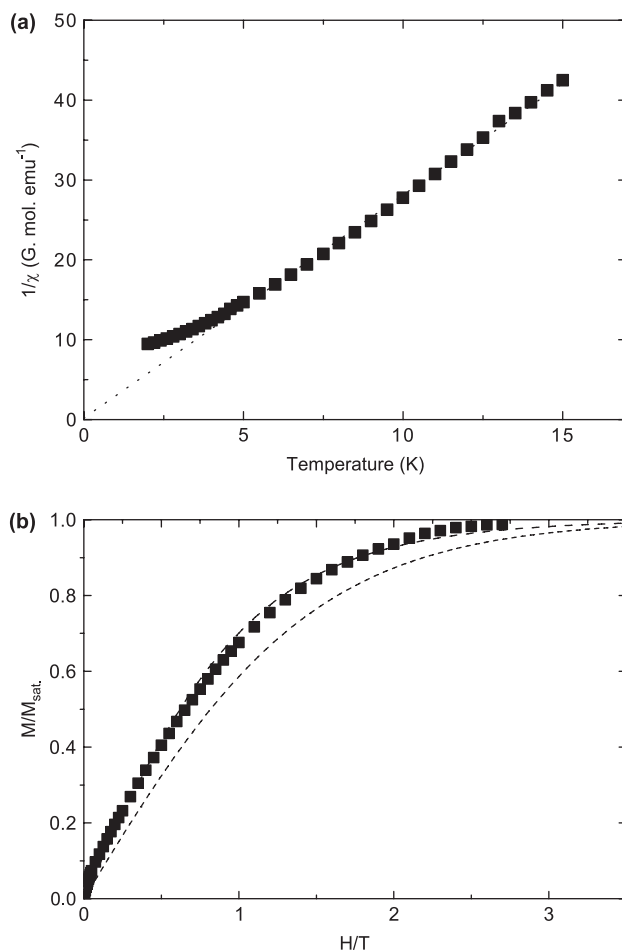
Figure 7. (a) Details of the 'Curie' plot ($1/\chi$ vs T) of solid **12$^{2•+}$** 2BF$_4^-$ between 2 and 15 K. (b) Normalized magnetisation against field over temperature (M/M_{sat} vs H/T) at 2 K compared to Brillouin function for $S=1$ (upper, solid line) and $S=1/2$.

probably due to weak intermolecular antiferromagnetic interactions (the relevant detail of the plot is shown in Fig. 7a). The plot of M/M_{sat} versus H/T fits a Brillouin function for a triplet, $S=1$ as shown in Figure 7b. As with other aza analogues of the Schlenk hydrocarbon,[36] the ground state **12$^{2•+}$** is a triplet.

2.4. Attempted four-electron oxidation of the tetraamines 13 and 14

The CVs of the tetraamines **13** and **14** are similar to those obtained for the diamine **12** in that the intermediate radical cations rapidly dimerise and that it is very difficult to remove all four electrons. As shown in Table 1, the first oxidation potential for compound **13** is similar to that of the diamine **12** but that of **14** is a little higher since the electrophore has one less stabilising methoxy substituent.[23] Small new peaks build up during repeated cycles corresponding to benzidines.[21–25]

Parallels to the diamine **12** also emerge in the UV/visible/near IR spectroscopic studies. When a solution of the tetraamine **13** is treated with 1 equiv of THBF$_4$, the absorption band at 4.13 eV decreases by about a quarter of the maximum expected and further upon addition of the second equivalent of oxidant. Upon addition of the third and fourth

equivalents of oxidant there is almost no change. The monoradical cation $13^{\bullet+}$ and diradical dication $13^{2\bullet+}$ are formed but $THBF_4$ is not a sufficiently strong oxidant to remove the third and fourth electrons. The tetraamine **14** behaves very similarly. Attempts to establish that high-spin species were formed by the oxidation of **13** or **14** with excess $NOBF_4$ followed by rapid solvent removal (using the same procedure as for the magnetometry studies of **12**) all failed. Only $S=1/2$ species can be detected. It seems either that the requisite polycations cannot be formed using $NOBF_4$ or that they dimerise much more rapidly.

3. Discussion

As shown in Figure 8, amminium ion analogues of non-Kekulé systems can either be coextensive or disjoint.[4,14,15] As we have shown in earlier studies of the 3,4′-through biphenyl system $15^{2\bullet+}$ and 3,3′-through biphenyl system $16^{2\bullet+}$, when hole distributions are coextensive the hole–hole repulsion is bigger than in the equivalent disjoint structure.[17] In the case of the coextensive 3,4′-through biphenyl system **15** this leads to difference between the first and second oxidation potentials of ∼0.1 V. In the coextensive 1,3-

through benzene system **12** the charge distributions are centred closer together and they overlap much more leading to a difference between the first and second oxidation potentials, which is >0.47 V. Since the tetraamines **13** and **14** are structurally very similar to **12**, and since for these the differences between first and second oxidation potentials are only 0.14 V and 0.18 V, we can safely argue that the dication diradicals $13^{2\bullet+}$ and $14^{2\bullet+}$ have the disjoint structures shown in Figure 8. In these the charges are far apart from each other as possible and there is no overlap in the hole distributions. (In the case of $13^{2\bullet+}$ this would also be the favoured structure since the electrophore with two methoxy substituents is slightly easier to oxidise than that with just one.) They would all be low spin species. The formation of high-spin coextensive species such as $12^{2\bullet+}$, $13^{3\bullet+}$, $13^{4\bullet+}$ or $14^{3\bullet+}$, $14^{4\bullet+}$ involves oxidation potentials >1.3 V. The oligomers $13^{n\bullet+}$ and $14^{n\bullet+}$ are good models for the equivalent polymers and the problems that are likely to be encountered. When a neutral polyarylamine is doped, the sites of doping are principally determined by electrostatics. Hence in the initial stages only disjoint radical ions (analogous to $5^{n\bullet+}$) will be formed first and the coextensive species (analogous to $5^{2n\bullet+}$), necessary to generate high-spin character, only generated in the final stages. Similarly, if doping is less than 100% efficient
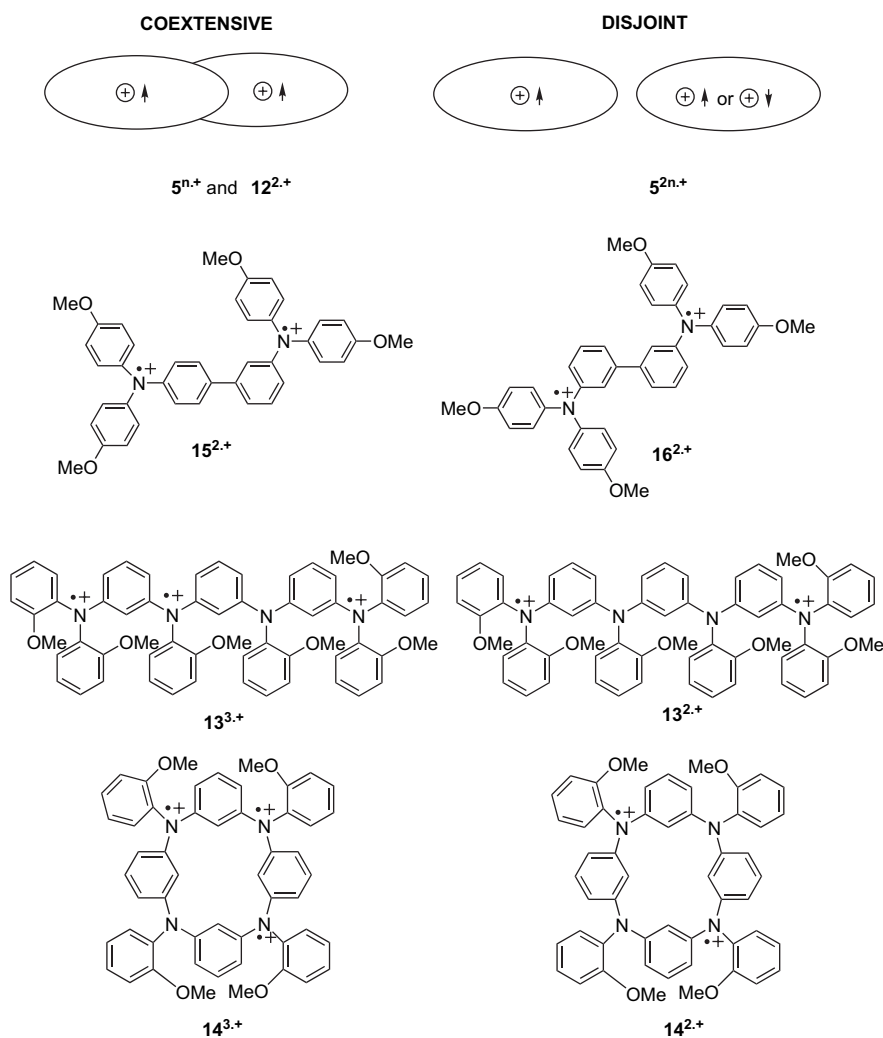

Figure 8. Coextensive (left) and disjoint (right) amminium radical cations and the most likely structures for the dications and trications formed from **13** and **14**.

and breaks in the spin-coupling network are generated it is clear that these will be disjoint discontinuities in the spin-coupling since this gives the greatest 'coulombic gain'. Obviously in polymers in which the spin-coupling is 3,4′-through biphenyl or 4,4″-through metaterphenyl, the coulombic 'penalty' for forming the coextensive radical ions will be less than in the models **12–14** where coupling is 1,3-through benzene. However, the exchange interaction will also be smaller and in the 4,4″-through metaterphenyl case it proves to be so small that there are problems of thermal population of low spin states.[13] Overall, despite the fact that it is easier to make triphenylamminium radical cations than trityl radicals and in general they are more stable, these coulombic effects make the triphenylamminium radical cation a less desirable base for high-spin polymers than the trityl radicals. Despite several years of work by several different groups, the best triphenylamminium radical cation based high-spin polymers only show clusters of 6–8 ferromagnetically coupled spins,[4,5,9,10] whereas the best trityl radical based high-spin polymers show up to ∼5000 ferromagnetically coupled spins.[2]

4. Experimental

4.1. Synthesis: general procedures

Full details of the syntheses, purification,[37] analytical and spectroscopic procedures are given in Supplementary data. The proof of the structure for the compounds (particularly for the key tetraamines **13** and **14**) rests substantially on 2-D NMR, COSY, HMQC and HMBC experiments, which were used to assign all the carbon and hydrogen resonances.[38]

4.2. X-ray crystallography

Single crystals of N,N,N',N'-tetrakis(2-methoxyphenyl)-benzene-1,3-diamine (**12**) were obtained by recrystallisation from dichloromethane/hexane. A crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer. $C_{34}H_{32}N_2O_4$, $M=532.62$, monoclinic, $a=9.4847(2)$ Å, $b=12.0494(2)$ Å, $c=24.2743(6)$ Å, $U=2772.0(1)$ Å^3, $T=100(2)$ K, space group $P2_1/n$ (no. 14), $Z=4$, $\mu=0.084$ mm^{-1}, 23,023 measured reflections, 5425 unique (R(int)=0.058). The final $wR(F_2)$ was 0.220 (all data).

4.3. Cyclic voltammetry

These studies were carried out using a conventional three electrode system coupled to an EG&G Model 362 scanning potentiostat and the system was controlled by a PC unit running the 'Condecon 320' cyclic voltammetry software. The working electrode was a small platinum disc, ca. 2 mm diameter, the counter electrode was a platinum coiled wire and the reference electrode, a silver wire immersed in a saturated lithium chloride/dichloromethane mixture containing the supporting electrolyte tetrabutylammonium hexafluoroborate (0.1 M). Prior to use, solvents were thoroughly dried and degassed, and the concentrations for the polyamines were approximately 1 mg cm^{-3}. The ferrocene/ferrocenium couple was used as a standard (taken to be +0.5 V vs Ag/AgCl under these conditions) and its oxidation potential

was checked before and after each experiment for the solvent used. The appropriate IR compensation was applied using the CONDECON software system. For the voltammograms shown in Figure 3, the potential was swept in the anodic direction (upper trace) and the lower trace represents the reverse sweep in the cathodic direction.[39]

4.4. UV/visible/near IR spectroscopy

The UV spectrum of a dilute polyamine solution (ca. [6/number of dopable sites]$\times 10^{-5}$ mol l^{-1}) in dry dichloromethane (3 cm^3) in a 1 cm path length cell was recorded in the range of 1600–250 nm. The spectrum was then recorded after each successive addition of THBF$_4$[38] (2.3×10^{-3} mol l^{-1}, 5–10 µl) in dichloromethane. This was done until 2 equiv of the oxidant per dopable site had been added. Software corrections were then employed to compensate for the small dilution caused by the addition of the oxidant. Compound **11**: λ_{max} 305 nm, 4.07 eV (log$_{10}$ ε, 4.08). Compound **11$^{•+}$**: λ_{max} 347 nm, 3.58 eV (log$_{10}$ ε, 3.80); 370, 3.36 (3.85); 512 (s), 2.44 (3.18); 594, 2.09 (3.46); 816 (s), 1.50 (3.48); 922, 1.35 (3.54). Isosbestic points **11/11$^{•+}$**, 273 nm; 320. Compound **12**: λ_{max} 300 nm, 4.16 eV (log$_{10}$ ε, 4.67). Compound **12$^{•+}$**: λ_{max} 381 nm, 3.25 eV (log$_{10}$ ε, 4.35); 473 (s), 2.63 (3.62); 594, 2.09 (3.46); 901 (s), 1.38 (3.56); 1107, 1.13 (3.47). Isosbestic points **12/12$^{•+}$**, 271 nm, 331, 486. Compound **13**: λ_{max} 301 nm, 4.13 eV (log$_{10}$ ε, 4.79). Compound **13$^{•+}$**: λ_{max} 385 nm, 3.25 eV (log$_{10}$ ε, 4.26); 452, 2.73 (4.03); 987 (s), 1.24 (3.65); 1149, 1.06 (3.75). Compound **13$^{2•+}$**: λ_{max} 369 nm, 3.33 eV (log$_{10}$ ε, 4.38); 447, 2.80 (4.13); 987, 1.24 (3.78); 1072, 1.08 (4.05). Compound **14**: λ_{max} 300 nm, 4.15 eV (log$_{10}$ ε, 4.76). Compound **14$^{•+}$**: λ_{max} 388 nm, 3.20 eV (log$_{10}$ ε, 4.18); ca. 1150, 1.18 (2.88). Compound **14$^{2•+}$**: λ_{max} 360 nm, 3.44 eV (log$_{10}$ ε, 4.39), ca. 1150, 1.18 (3.18).[40]

4.5. Electron paramagnetic resonance

EPR measurements were made on an X-band ER-200 Bruker ESR spectrometer using either a simple standard EPR tube or a sealed cell that enabled the sample to be concentrated or diluted under vacuum. In a typical experiment, the EPR tube was filled with a thoroughly dried and degassed solution of the polyamine ca. 1×10^{-4} mol l^{-1} in dichloromethane, so that the depth of the solution in the tube spanned the microwave cavity (ca. 0.5 cm^3). The solution was cooled to -77 °C and NOBF$_4$ (20-fold excess) was added to the cold solution under a steady stream of argon. The solution was sonicated for 15 min using a Kerry ultra-sound bath operating at 50 Hz under a dry atmosphere of argon.

4.6. Magnetometry

Magnetic measurements were carried out using a SQUID magnetometer (MPMS, Quantum Design) at the University of Sheffield. In a typical experiment NOBF$_4$ (1 g, 8.6 mmol, 40 mol %) was added to a thoroughly dried and degassed stirred solution of polyamine (100 mg, ca. 0.2 mmol of dopable nitrogen sites) in dichloromethane (300 cm^3) at 0 °C under an atmosphere of dry argon in a round-bottomed Schlenk flask. The solution was sonicated for 30 min using a Kerry ultra-sound bath operating at 50 Hz under an argon atmosphere at 0 °C. Most of the solvent was

rapidly removed under vacuum and the sample fully dried at ca. 10^{-4} mm of Hg. The flask was taken into a glove box, and using a plastic spatula, the solid residue was transferred into a plastic capsule. The sample was mounted in a straw that serves as part of a sample holder, and transferred via an argon filled tube into the magnetometer where it was maintained under an atmosphere of helium. After the measurements were made, the oxidised sample was submitted for combustion analysis with minimum exposure to the air. The magnetisation data shown were corrected for the diamagnetism of the sample holder, quartz cell and excess reagent (ca. 1 emu G^{-1}).

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Supplementary data

This contains additional cyclic voltammetry, UV/visible/near IR data, the preparative procedures, and an example of NMR data used in the complete assignment of all resonances in the ^{1}H NMR and ^{13}C NMR spectra (of *N,N'*-bis(2-methoxyphenyl)benzene-1,3-diamine **8**). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.08.038.

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38. Details are given in Supplementary data.

39. Further traces are given in Supplementary data.

40. Spectra are shown in Supplementary data.