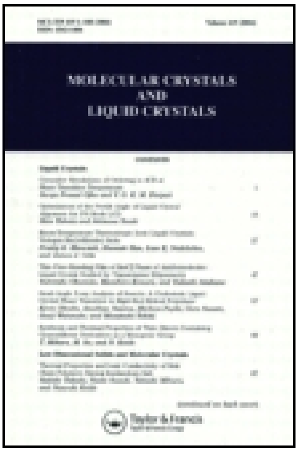

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Synthesis and Oxidation of Di-, Tri-, Tetra-, and Pentaamines

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SYNTHESIS AND OXIDATION OF DI-, TRI-, TETRA-, AND PENTAAMINES

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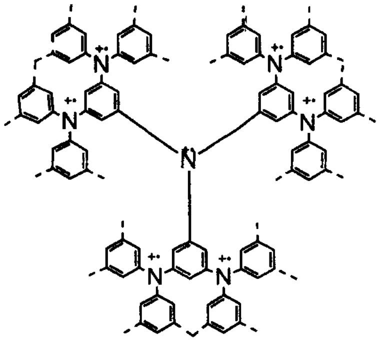
Abstract A series of di-, tri-, tetra-, and pentaamines were synthesized as precursors of corresponding aminium radical-cations. Redox properties of these amines were studied by cyclic voltammetry and aminium radical-cations obtained by chemical oxidation of these amines were investigated by ESR and UV-VIS spectroscopy.

INTRODUCTION

Triarylaminium radical-cations with substituents at *para*-positions of aromatic rings are known as one of stable radicals which can be isolated under atmospheric conditions.[1] Therefore, they have been considered as promising candidates for spin centers of high spin polyradicals proposed by Mataga *et al.*[2] Though oxidation of poly(*m*-aniline) would generate high spin organic molecules which employ -N•- as radical centers if oxidation proceeds ideally and there have been several attempts of preparation.[3] Star burst type poly(aminium radical-cations) such as **1** can also be regarded as candidates for stable high spin organic molecules with large magnetic momentum at high temperature. As a high spin aminium radical-cation, triaminium **2** has been reported by Yoshizawa *et al.* to be quintet with unusual stability in spite of absence of *para*-substituents.[4] We



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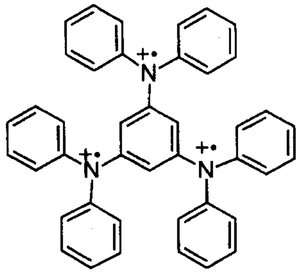

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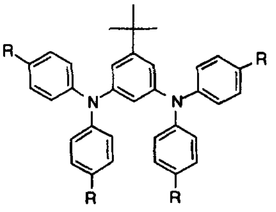
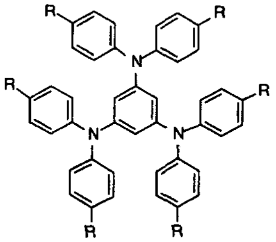
started systematic study on the aminium radical-cations to elucidate possibility of poly(aminium radical-cation) **1** and synthesize high spin aminium radical-cations which can be isolated and stable at room temperature. Systematic investigation on oligomeric structures of polyradicals is one of the most promising way to high spin organic molecules.

SYNTHESIS OF DI-, TRI-, TETRA-, AND PENTAAMINES

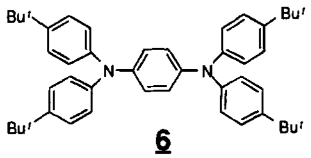
As substructures of **1**, di- (**3a**, **3b**), tri- (**4a**, **4b**), and pentaamines (**5**) were prepared, diamine **6** and tetraamine **7** with different topology were prepared for comparison.[5] Amines **3a**, **3b**, **4a**, **4b**, **6**, and **7** were synthesized by the coupling between aryliodide and *in situ* prepared copper amide (eq. 1).[6] Pentaamine **5** was synthesized from



3a: R = *t*-butyl
3b: R = -OCH$_3$



4a: R = *t*-butyl
4b: R = -OCH$_3$



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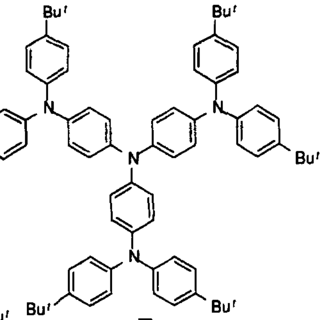

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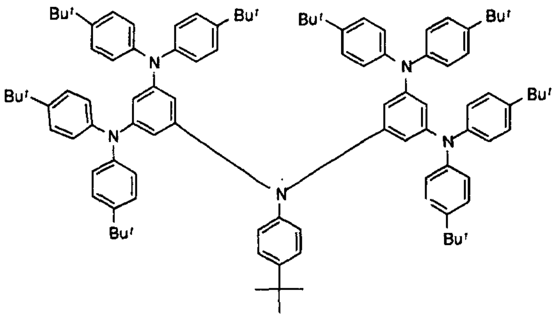

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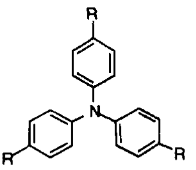


8a: R = *t*-butyl
8b: R = -OCH$_3$

$$\mathrm{Ar_2NH} \xrightarrow[\mathrm{CuI\,/\,THF}]{\mathrm{BuLi}} [\mathrm{Ar_2NCu}] \xrightarrow{\mathrm{Ar'I\,/\,pyridine}} \mathrm{Ar_2Ar'N} \qquad (1)$$

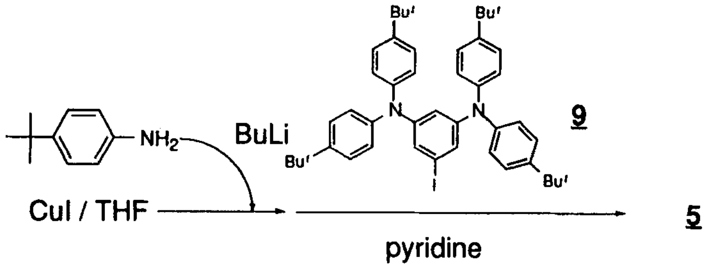
4-*t*-butylaniline and the iodide **9** under the similar conditions (eq. 2). Structure of these amines were confirmed by ^{1}H and ^{13}C NMR, FAB-MS, and elemental analysis.

CYCLIC VOLTAMMOGRAMS OF DI-, TRI-, TETRA-, AND PENTAAMINES

To investigate redox properties, cyclic voltammetry of mono-(**8a**, **8b**), di-(**3a**, **3b**, **6**), tri-(**4a**, **4b**), tetra-(**7**), and pentaamines (**5**) was carried out (FIGURE 1). Cyclic voltammograms of diamines **3a** and **3b** consist of two steps quasi-reversible oxidation to di(radical-cation) followed by further irreversible oxidation. Redox waves of triamines are less reversible than diamines. Only oxidation to mono(radical-cation) is clear and large irreversible waves appear after the second oxidation wave. A cyclic voltammogram of pentaamine **5** consists of two clear but irreversible oxidations followed by large irreversible oxidation waves. On the other hand, *para*-connected amines **6** and **7** showed far clear voltammograms. The voltammograms of **6** and **7** consist of two and four steps reversible waves, respectively.

ESR AND UV-VIS STUDY OF OXIDATION OF DI-, TRI-, AND PENTAAMINES

Mono-(**8a**, **8b**), di-(**3a**, **3b**), tri-(**4a**, **4b**), and pentaamines (**5**) were oxidized by $AgClO_4$ (in CH_2Cl_2), $SbCl_5$ (in CH_2Cl_2), or I_2 (in toluene) and studied by ESR and UV-VIS spectroscopy. Oxidation of these amines by $AgClO_4$ (in CH_2Cl_2) or $SbCl_5$ (in CH_2Cl_2) led to blue solution and generation of aminium radical-cations was confirmed by the absorption corresponding to the blue color, e. g. 682 nm for **8a**, 860 nm for **3a**, 815 nm for **4a**, and 886 nm for **5** in $AgClO_4$ / CH_2Cl_2, respectively. Mono(radical-cations $\mathbf{8a}^{+\bullet}$ and $\mathbf{8b}^{+\bullet}$ showed typical ESR spectra of aminium radical-cations at room temperature, e. g. $g = 2.0038$ and $a_N = 0.985$ mT for $\mathbf{8a}^{+\bullet}$. The spectra changed to triplet due to anisotropy of g-value and/or hyperfine coupling when cooled to 77 K (FIGURE 2). In the oxidation of diamines **3a** and **3b** , oxidation process from mono(radical-cation) to di(radical-cation) (FIGURE 3) or decomposition or further oxidation process from di(radical-cation) to mono(radical-cation) (FIGURE 4) were observed according to the amount of oxidant. However, measurements at 77 K or lower temperature gave only a single line and $\Delta m_s = 2$ transition was not observed. Oxidation of triamine **4a** and **4b** also resulted in ESR spectra with structures probably attributable to hyperfine structures by nitrogen and spin-spin exchange, but frozen solutions of them at 77 K did not show expected fine structures and $\Delta m_s = 2$ transitions (FIGURE 5). The



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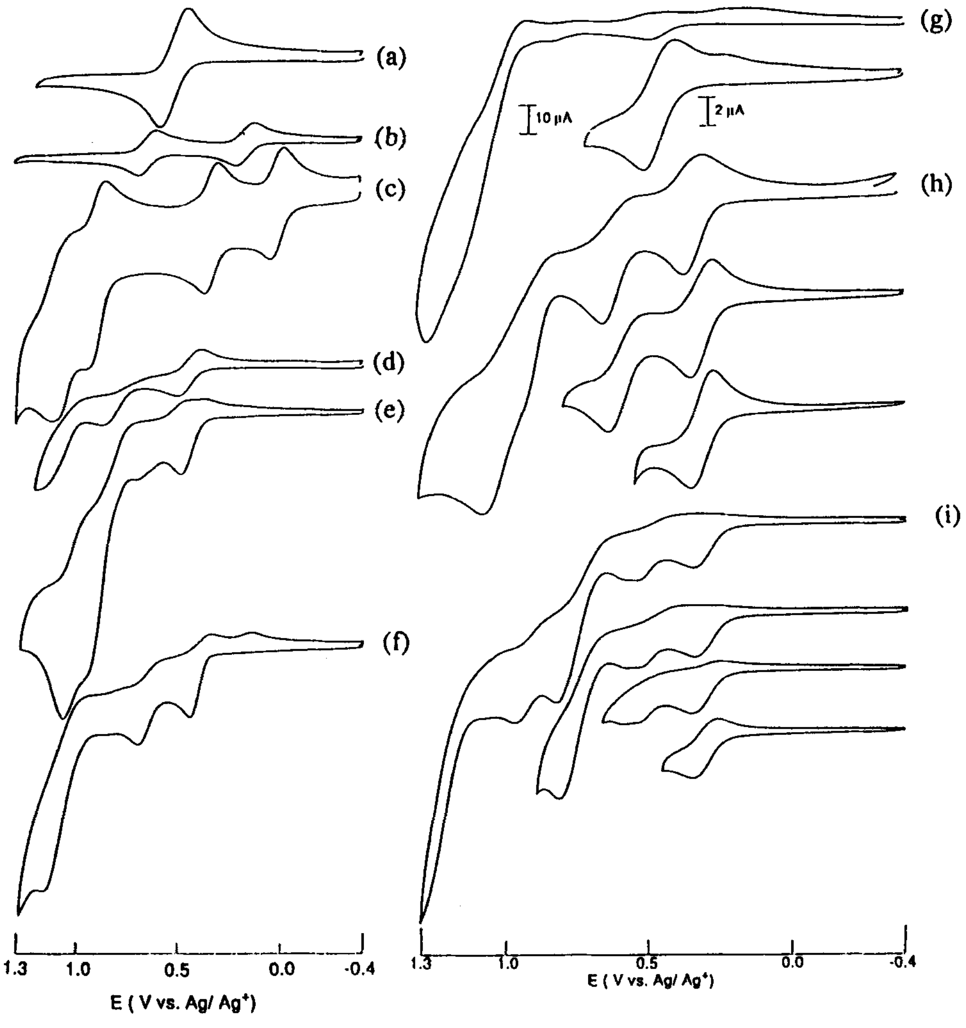


FIGURE 1. Cyclic voltammograms of (a) **8a**, (b) **6**, (c) **7**, (d) **3a**, (e) **4a**, (f) **5**, (g) **8b**, (h) **3b**, (i) **4b** in dichloromethane with 0.10 M *n*-Bu_4NClO_4 as supporting electrolyte. Working electrode; glassy carbon, counter electrode; Pt, reference electrode; Ag / 0.01 M $AgNO_3$ / 0.10 M *n*-Bu_4NClO_4 / CH_3CN, scan rate; 30 mVs^{-1}.

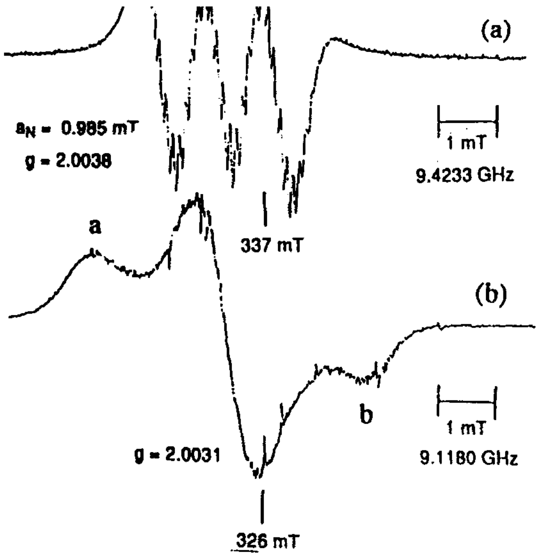


FIGURE 2. ESR spectra of **8a** / $AgClO_4$ / CH_2Cl_2. (a) 290 K. (b) 77 K. Difference between a and b is 4.52 mT.

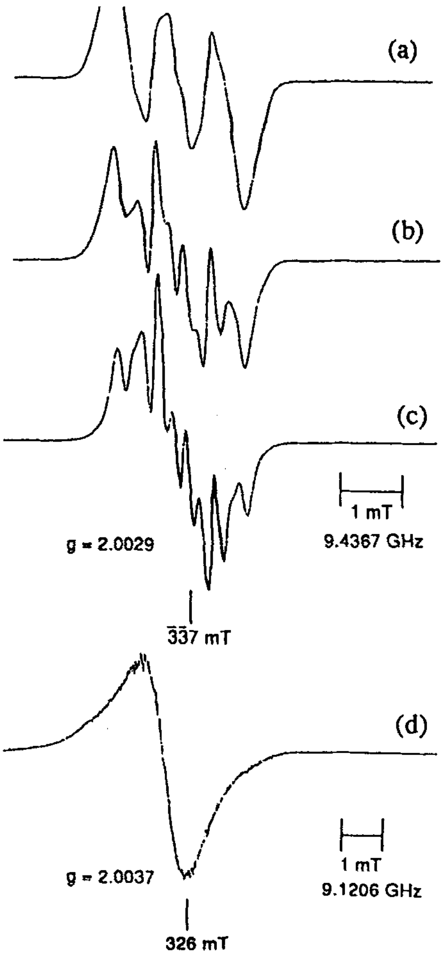


FIGURE 3. ESR spectra of **3a** / $SbCl_5$ / CH_2Cl_2. (a) 290 K. (b) after 15 min. (c) after 30 min. (d) (c) was cooled to 77K.

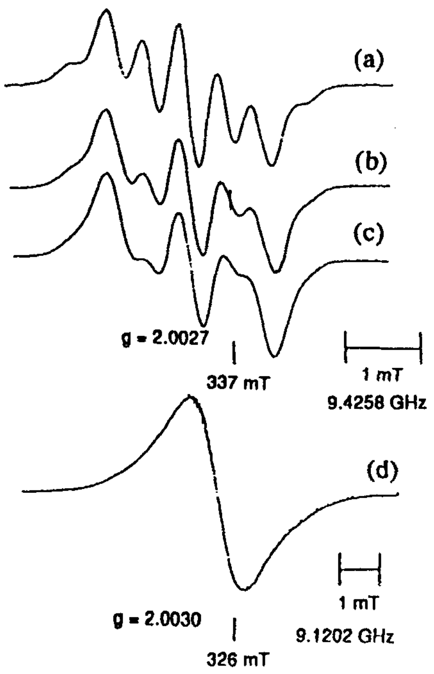


FIGURE 4. ESR spectra of **3a** / $AgClO_4$ / CH_2Cl_2. (a) 290 K. (b) after 10 min. (c) after 20 min. (d) (a) was cooled to 77K.

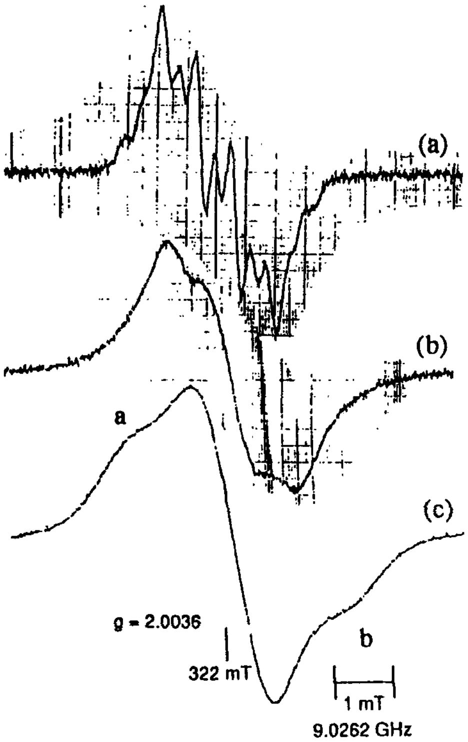


FIGURE 5. ESR spectra of **4b** / I_2 / toluene. (a) 290 K. (b) 190 K. (c) 63 K. Difference between a and b is 3.87 mT.

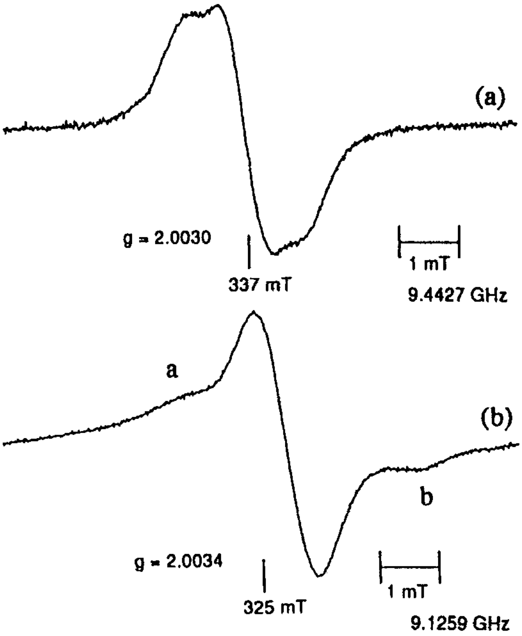
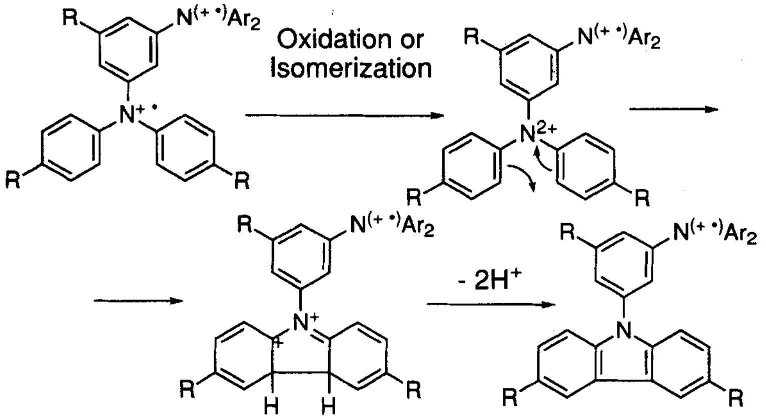


FIGURE 6. ESR spectra of **5** / $SbCl_5$ / CH_2Cl_2. (a) 290 K. (b) 77 K. Difference between a and b is 4.02 mT.

blue solution of **5** / $SbCl_5$ / CH_2Cl_2 did not give well resolved spectrum and two shoulders were observed at 77 K (FIGURE 6). Sometimes, ESR spectra of oxidation of these amines at frozen solution state showed two shoulders (FIGURE 5, 6), but we could not assign these as fine structures because the positions of them were very close to those observed in **8a**$^{+\bullet}$ and **8b**$^{+\bullet}$(FIGURE 2).

DISCUSSION

Although aminium radical-cations such as **8a**$^{+\bullet}$ and **8b**$^{+\bullet}$ are known as stable radicals, redox behavior of *meta*-connected di-, tri-, and pentamines was more complex than expected. According to cyclic voltammograms, oxidation to the corresponding di-, tri-, and penta(radical-cations) was irreversible and further oxidation process was observed. Concerning electrochemical oxidation process of triarylamines, further oxidation of aminiums such as **8a**$^{+\bullet}$ and **8b**$^{+\bullet}$ at higher potential was reported[7] to lead to formation of a one-center dication followed by cyclization to a carbazole (eq. 3) and further oxidation. The second irreversible oxidation was observed around 0.9 V for **8b** and higher than 1.3 V for **8a** (FIGURE 1). In diamine **3a** and **3b**, the first and second waves are assigned to oxidation to mono(radical-cation) and di(radical-cation),



(3)

respectively, and the third oxidation wave is regarded as formation of trication followed by side reactions such as generation of carbazoles. Although the cyclic voltammograms of **3a** and **3b** support generation of the desired di(radical-cations), careful oxidation is necessary to avoid further oxidation. In triamine **4a** and **4b** and pentaamine **5**, redox processes are more complex, probably because of instability of the corresponding radical-cations. Though the oxidation potential of **8a** to the dication is higher than 1.3 V, rotation of one of the N-Ar bonds in di- or tri(radical-cation) would result in isomerization to the molecule with one center dication moiety and further reaction described above (eq. 3) would occur. Thus, the cyclic voltammetry data do not support clean formation of the corresponding radical-cations. ESR data obtained so far are consistent with cyclic voltammetry data. Oxidation of diamine **3a** monitored by ESR clearly showed oxidation to the di(radical-cation) via mono(radical-cation) and further oxidation or decomposition. However, we could not assign generated species in the oxidation of triamines **4a**, **4b**, and pentaamine **5** because of complex or unresolved ESR spectra at room temperature and lack of resolved fine structures in frozen solutions. Although we planned to assign spin multiplicity by fine structures of ESR spectra, resolved fine structure was not obtained because of 1) failure of matrix isolation due to aggregation , 2) smaller anisotropy of fine structure than anisotropy of g-value or hyperfine structure, 3) distribution of D and E values due to conformational isomers, and/or 4) failure of generation of desired species. To obtain stable di-, tri-, and penta(radical-cations) with simple redox behavior, synthesis of these amines with further steric protection such as *ortho*-substituents is under investigation.

CONCLUSION

Meta-connected di-, tri-, and pentaamines were synthesized by the coupling between *in situ* prepared copper amide and aryliodide as precursors for the corresponding aminium radical-cations. However, cyclic voltammograms and chemical oxidation monitored by ESR revealed complex redox processes of these amines and clear fine structure have not yet been obtained so far. More synthetic effort is necessary to construct a series of high spin aminium radical-cations.

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