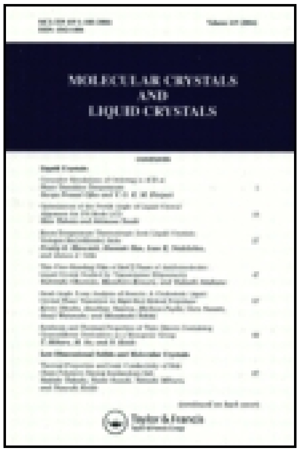

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MODELS FOR CHARGED ORGANIC HIGH-SPIN SYSTEMS; SYNTHESIS AND CYCLIC VOLTAMMETRY OF ONE- AND TWO-DIMENSIONAL DIARYLAMINOBENZENES

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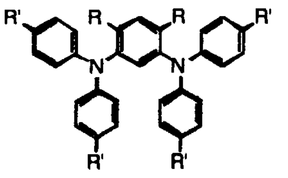
Abstract A series of 1,3-di(diarylamino)benzenes (DABs) and 1,3,5-tris(diarylamino) benzenes (TABs) were synthesized as model precursors for polycationic π-conjugated high-spin systems. CV measurement at low temperature showed that the chemical stability in solution of mono- and polycationic oxidation states of the various DABs and TABs derivatives depend on their structures. Correlation between the chemical stability of these cations and their molecular structure is discussed.

INTRODUCTION

During the last decade, spin manipulation in chemistry underlying molecule-based magnetism developed to bring diverse intriguing topics in the pure and applied sciences. Among those, charged organic high-spin systems of elaborate molecular designs based on through-bond topological symmetry have emerged as models for charge fluctuation vs. spin polarization. Until recently, a few examples of charged homoatomic high-spin hydrocarbon were reported.[1,2] On the other hand, heteroatomic organic high-spin systems with charges have only recently emerged and "topology rules" for spin alignment in π-conjugated heteroatomic systems have been examined.[3-7]

Since *para*-substituted triphenylaminium cations are known to be charged persistent radicals, *meta*-linked poly-diarylaminobenzenes are promising as positively charged stable high-spin molecules. Yoshizawa *et al.* reported the oxidation states of *N,N,N',N',N'',N''*-hexaphenyl-1,3,5-triaminobenzene.[3] Also Blackstock *et al.* reported the generation of mono-, di- and trication of *N,N,N',N',N'',N''*-hexa(4-anisyl)-1,3,5-

triaminobenzene, which are stable at low temperature(<-40℃).[4] The latter group claimed the chemical instability of non-substituted 1,3,5-triaminobenzene in the polycationic states in solution. In this work, 1,3-di(diarylamino)benzenes (DABs) (**3**) and 1,3,5-tris(diarylamino)benzenes (TABs) (**4**) have been considered as models for precursors of 1D and 2D positively charged organic high-spin systems, respectively. Polyoxidation states of **3** have been for the first time examined as models for 1D hyperbranched π-aryl based amines.



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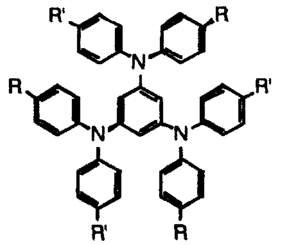

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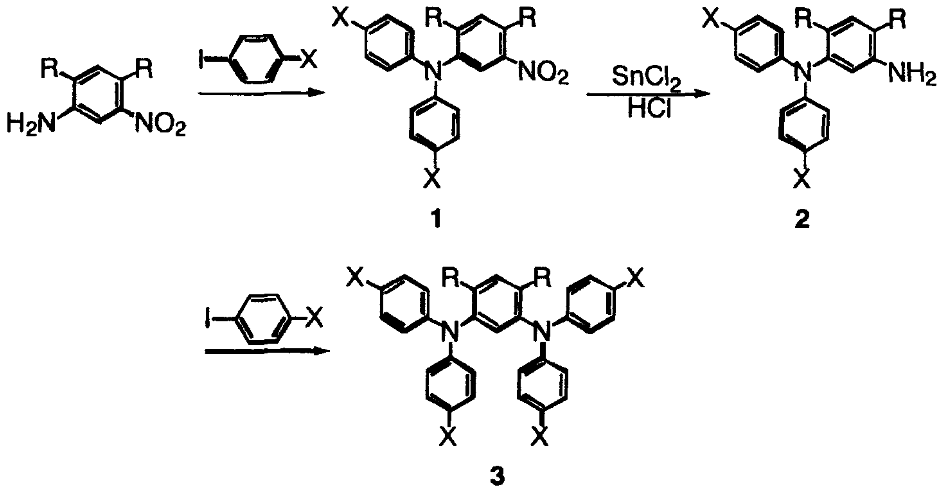
It is essential for molecular designs of stable charged organic high-spin systems to elucidate correlation between their chemical stability of corresponding polycations and their molecular structure. Here we report on synthesis and redox properties of **3** and **4**.

SYNTHESIS OF DABS AND TABS



Scheme 1

3 were synthesized using succesive Ullmann couplings. The synthetic routes are as follows; *m*-nitroanilines were reacted with *p*-substituted iodobenzenes at 180℃ for 12h to afford *m*-nitrotriphenylamines (**1**) in 20-70% yield. After reduction of **1** with $SnCl_2/HCl$ (yield 80-90%), resulting diamines (**2**) were reacted with *p*-substituted iodobenzenes at 180℃ for 12h and obtained crude products were purified with column-chromatography (silica gel, $CHCl_3$) to afford **3** in 5-50% yield. Total yields of **3** are summarized in Table I. Unfortunately, Ullmann couplings with *m*-dibromobenzenes and diphenylamines gave complex mixtures which could not be purified.

TABLE I Total yields of 3

Entry	R	X	Yield (%)[a]
3a	H	C_2H_5	8
3b	H	CH_3	44
3c	H	H	29
3d	H	F	18
3e	H	Cl	5
3f	CH_3	OCH_3	13
3g	CH_3	CH_3	11
3h	CH_3	H	30

a) Isolation yield

A series of **4** were synthesized according to the method reported by Ishikawa *et al*.[8] and yields are summarized in Table II.

TABLE II Total yields of 4

Entry	R^1	R^2	Yield (%)[a]
4a	OCH_3	OCH_3	23
4b	OCH_3	CH_3	34
4c	CH_3	CH_3	30
4d	H	H	51
4e	F	F	47
4f	Cl	Cl	53
4g	H	OCH_3	64
4h	H	CH_3	42
4i	H	F	24
4j	H	Cl	29
4k	H	CF_3	11

a) Isolation yield

CV MEASUREMENT OF DABS AND TABS

In order to investigate the stability of mono- and di-cations of **3**, cyclic voltammetry measurements were made in *n*-butyronitrile containing 0.1M of *n*-Bu_4NBF_4 and 0.001M of **3**, using Ag/Ag^+ as a reference electrode. For **3c** which has no protecting group, corresponding monocation was very unstable, so only the first oxidation peak was observed and corresponding reduction wave could not be observed even at -78℃ with a scan rate of 100mV/s (Fig. 1).

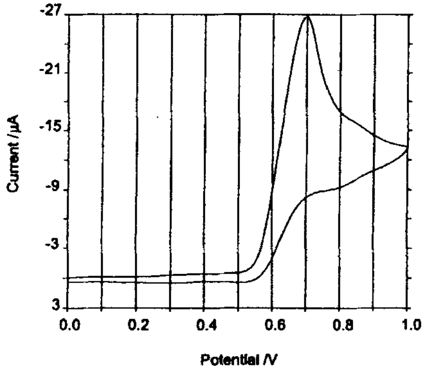


FIGURE 1 CV curve for **3c** at -78℃

3a,b,d and **e** which have four substituent groups at *p*-positions of outer four phenyl rings also showed the same behavior at the same condition. So these **3a-e** will not be expected to form stable polycationic high-spin molecules. First oxidation potential for **3a-e** and **h** are shown in Table III.

TABLE III Peak potentials for the first oxidation process of **3a-e** and **h** in PrCN(0.1M-Bu_4NPF_6 at -78℃)[a]

3	3a	3b	3c	3d	3e	3h
Eox1(mV)	559	573	699	765	802	694

a) Potentials vs. a Ag/Ag^+ relative electrode with a scan rate of 100mV/s

In contrast, for **3f** and **g**, chemical stability of the corresponding mono- and di-cations are remarkably enhanced. Even at ambient temperature, two reversible redox couples (Ipc/Ipa ≒ 1) were observed, as shown Figure 2. Redox potentials $E^{0'}$ and ΔE_p for **3f** and **3g** are shown in Table IV, respectively. For **3h**, however, only a single irreversible

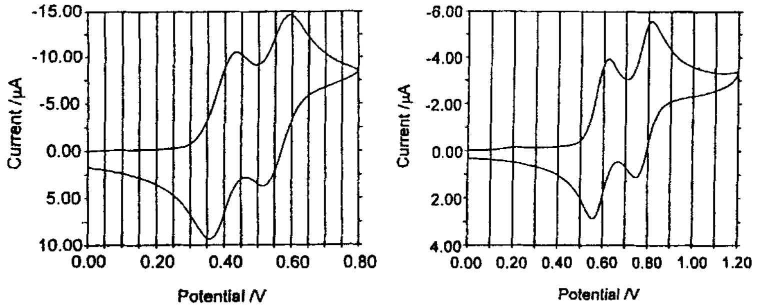


FIGURE 2 CV curves for **3f** (left) and **3g** (right) at 25℃

TABLE IV Redox potentials ($E^{o'}$)^{a} for **3f-g** in PrCN at 25℃^{b}

3	3f		3g	
$E^{o'}$(mV)	395	556	591	782
ΔE_p(mV)	79	74	62	65

a) Potentials vs Ag/Ag^{+} $E^{o'}=(E_{pa}+E_{pc})/2$

b) PrCN containing 0.1M $n\text{-}Bu_4NPF_6$ was used and the scan rate was 100mV/s.

oxidation wave was observed. These results suggest that the protecting groups at particular sites of both central and outer phenyl rings are essential for stabilizing mono- or di-cation of **3**.

Also for **4**, redox properties were examined. For **4d** which has no protecting group, corresponding mono-cation was unstable even at -78℃. For **4c** and **e-k** which have three or six protecting groups at *p*-positions of outer phenyl rings, only the first redox couple was reversible. For **4a-c** which have at least three methoxy groups, three pairs of reversible redox couples were observed.

CONCLUSION

we have established (1) the synthetic route for **3** which is a prototypical example for one-dimensional positively charged high-spin molecules and we have examined (2) the strategy for elaborate molecular design of the stable oxidation states of **3** and **4**. The syntheses of *m*-,*m'*-diarylaminotriphenylaminobenzene derivatives and higher homologous are in progress.

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