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ScienceDirect

Polyhedron 26 (2007) 2008–2012

POLYHEDRON

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Amine-based organic high-spin systems: Synthesis, electrochemical and spectroscopic studies of polyalkylated one-dimensional oligoaryl triamines

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Received 22 September 2006; accepted 23 September 2006

Abstract

A polyalkylated triamine, 2,2′,4,4′-tetrabromo-4″-methyl-5,5′-bis(di(3,4-di-methylphenyl)amino)triphenylamine, was designed and successfully synthesized as a model precursor for purely organic cationic high-spin systems. Cyclic voltammetry measurement revealed that the triamine gives stable mono- and dicationic states and fairly unstable tricationic state. Novel electron transfer stopped-flow (ETSF) methods were invoked for characterizing the absorption spectra of the corresponding mono- and oligo-cationic states. The triplet state of the dication was confirmed by ESR spectroscopy.

Keywords: Oligoarylamines; Electrochemical methods; Electron transfer stopped-flow method; Charged high-spin systems; Stable organic open-shell systems; Polyalkylated derivative

1. Introduction

Recently, *meta*-connected oligoarylamines have been attracting much attention as model precursors for positively charged organic high-spin systems [1,2]. As plural electrons are required to be removed from neutral precursors in solution to give the corresponding high-spin states, the occurrence of the stable oxidized oligocationic states in solution are of crucial importance. Thus, some structural modifications are necessary in order to improve the stabilities of the oxidized states: particularly the stabilization enables us to make various physicochemical measurements. When our research started a decade ago, the short-term goal was detection of stable ground-triplet dications generated from oligoarylamines in solution. Monomeric triarylamines with various substituents at their *para*-positions are widely known to give extremely stable monocation radicals upon chemical or electrochemical oxidation [3]. Until now, extensive studies have been done on the design and synthesis of neutral oligoarylamine precursors by using these types of triarylamines as spin units [2]. However, as previously pointed out by Stickley et al. [2f], the stability of monomeric cation radical is not always a sufficient indicator of the stability of the corresponding oligo-cationic states of extended oligoarylamines. A relationship between the structures of oligoarylamines and the stabilities of their corresponding oligocations is the focus of the current issues to establish molecular design rules for extended oligoarylamine-based high-spin systems.

Previously, we reported that oligotriarylamines with two or three *meta*-connected diarylamino groups **1**, **2** (Fig. 1) give stable di- and trications upon multi-electron oxidation, respectively [2b,2c]. A novel electron spin transient

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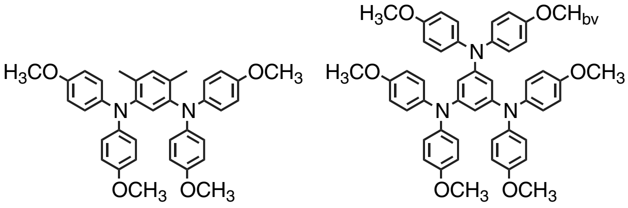
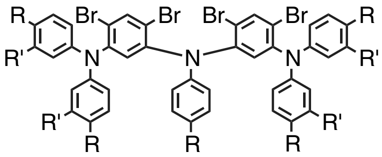
doi:10.1016/j.poly.2006.09.057



1 **2**

Fig. 1. Structures of N,N,N',N'-tetrakis(4-anisyl)-4,6-dimethyl-1,3-phenylene-diamine (**1**) and N,N,N',N',N'',N''-hexakis(4-anisyl)-1,3,5-phenylene-triamine (**2**).

nutation (ESTN) method was applied to the di- and trication, unequivocally identifying the spin multiplicities in their triplet and quartet ground state, respectively. In the designed molecules, four or six methoxy groups, i.e., strong electrodonating groups, are introduced to stabilize the di- or tricationic states, respectively. We have examined the relationship for a number of 1,3-bis(diarylamino)benzenes as exemplified by **1**, establishing the molecular design rules to obtain diamine-based stable triplet dications in the ground state. Thus, an elaborate molecular design for tricationic entities has been challenging issues for us. Although we reported that a two-dimensionally extended triamine gives the corresponding stable trication in solution at low temperature [2b], as one-dimensionally extended triamines, 3,3′-bis(diarylamino)triphenylamines emerge, which allow us to modify molecular structures more easily in terms of synthetic chemistry. Recently, Ito et al. have reported a highly brominated derivative **3** (Fig. 2), which gives the corresponding stable dication upon two electrons oxidation [2h]. However, they failed to detect the corresponding trication with polybromo substitutions. Their results encouraged us to design and synthesize compound **4**, which has five electrodonating methyl groups at the peripheral rings and four bromo groups at the central rings. Compound **4** is expected to yield more thermodynamically stable mono- and oligo-cations than those of **3** [2j]. The CV measurements of **4** showed the generation of both stable dication $\mathbf{4}^{++}$ and moderately stable trication $\mathbf{4}^{+++}$ at ambient temperature. The electron transfer stopped-flow (ETSF) method allowed us to study the spectroscopic properties of the mono-, di- and tricationic states of **4**. These results are the first report on detection of a one-dimensional oligoarylamine-based tricationic state. The enhancement of the thermodynamic and kinetic stability for oligo-cations of **4** is ascribed to the steric as well as electronic effects of the electrodonating methyl groups, which raise the HOMO energy level. The ESR study of the dication $\mathbf{4}^{++}$ showed that the ground state is spin-triplet. The trication $\mathbf{4}^{+++}$ was not stable enough in a time scale for the conventional ESR sampling, indicating that chemical modification was not successful enough to stabilize the tricationic states in solution.



3: R=Br, R'=H
4: R=CH$_3$, R'=H
5: R=R'=CH$_3$

Fig. 2. Structures of 3,3′-bis(diarylamino)triphenylamines (**3**–**5**).

In this study, we have redesigned and synthesized a new alkylated triamine **5** with nine methyl groups at the peripheral aromatic rings, which is expected to give thermodynamically more stable oligocationic states. The stabilities of the corresponding oligo-cationic states have been examined by using the cyclic voltammetry and ETSF method. The electronic states of the oligocationic states have been identified by cw-ESR measurements in rigid glass at low temperature.

2. Results and discussion

2.1. Synthesis of 2,2′,4,4′-tetrabromo-4″-methyl-5,5′-bis(di(3,4-dimethylphenyl)amino)-triphenylamine (5)

As shown in Fig. 3, compound **5** was synthesized and isolated as colorless powder by the similar method reported by Ito et al. [2h]. Benzyltrimethylammonium tribromide (BTMA · Br$_3$), a mild bromination reagent, has successfully been employed for the regioselective bromination at all *para*-positions of 3,3’-bis(diarylamino)triphenylamines [2h,2k]. As all *para*-positions of the peripheral rings are protected by methyl groups for **7**, only the *para*-positions of the central rings would be brominated. All new compounds were fully characterized by spectroscopic methods. Data only for **5** and **7** are given below. Compound **7**: ^{1}H NMR(CDCl$_3$): δ 2.13 (s, 12H), 2.18 (s, 12H), 2.24 (s, 3H), 6.51 (dd, 4H, $J = 8.0$, 1.6 Hz), 6.56 (dd, 4H, $J = 8.0$, 1.6 Hz), 6.75–6.78 (m, 6H), 6.89–7.00 (m, 10H). Compound **5**: In spite of repeated recrystallization, compound **5** exhibited a complicated ^{1}H NMR spectrum probably due to the restricted rotation of the nitrogen–aromatic ring bonds. HRMS: Calc.: 1017.0503 for $C_{51}H_{47}N_3Br_4$. Obsd.: 1017.0498.

2.2. Cyclic voltammetry measurements

For compound **5**, cyclic voltammetry in *n*-butyronitrile at ambient temperature revealed two chemically reversible one-electron transfers, indicating the corresponding stable mono- and dications in solution. However, upon further oxidation, an irreversible oxidation wave was observed, indicating the possible generation of the unstable trication. ($E_1^0 = 0.545$V, $E_2^0 = 0.702$V, $E_3^{ox} = 1.129$V, versus F_c/F_c^+) (Fig. 4). Comparing the first redox potential of **5** and **4** ($E_1^0 = 0.605$V versus F_c/F_c^+) [2k], **5** can be oxidized more easily, suggesting the elevated HOMO level due to polyalkylation. AM1 calculation also indicated that the HOMO energy level of **5** is higher than that of **4**.