Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Polyhedron 26 (2007) 2027–2030
POLYHEDRON
www.elsevier.com/locate/poly

m-Phenylenediamine-based high-spin dication diradicals: Analysis of the decomposed products

Masafumi Yano [a,*], Kengo Kitagawa [a], Masakazu Tatsumi [a], Kazunobu Sato [b], Takeji Takui [b]

[a] *Unit of Chemistry, Faculty of Engineering, Kansai University, Suita-shi, Osaka 564-8680, Japan*
[b] *Department of Chemistry, Graduate School of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan*

Received 22 September 2006; accepted 23 September 2006
Available online 29 September 2006

Abstract

A tetraaryl-*m*-phenylenediamine dication diradical in the triplet ground state was chemically generated and decomposed in preparative scale. The obtained mixture was separated and purified to examine the decomposed products. A nitro compound and a biaryl were formed as the main products, indicating the cleavage of the pi-conjugation. The relationship between the substituent influence and the structure of the decomposed products, and reaction mechanism are reported. These results serve for establishing guidelines for molecular designing of next-generation charged high-spin molecular systems such as oligoarylamine-based pluri-charged high-spin molecules, in a more sophisticated manner.

Keywords: Oligoarylamines; Charged high-spin systems; Dication diradicals; Decomposition reaction; Pi-system cleavage

1. Introduction

Over the last few decade, charged purely organic high-spin systems have been one of the controversial issues in high spin chemistry [1,2]. Several articles have been devoted to the study of positively charged high-spin systems generated by hole doping, which have been attracting much attention as models for studying an interplay between plurichárge fluctuation and spin polarization in π-electron networks. In this context, oligoarylamines, in which two or more nitrogen cores are *meta*-connected, are promising precursors [2]. Since the precursors have topologically *pseudo*-degenerate HOMOs, the corresponding oligocationic states formed upon plural-electron removal are expected to exhibit high spin multiplicities in the electronic ground state. Previously, we reported that oligotriarylamines with two or three *meta*-connected diarylamino groups (**1**, **2**) (Fig. 1) exhibit a stable triplet or quartet ground state upon multi-electron oxidation, respectively [2b,2c]. Similar oligoarylamine-based derivatives were also reported by other groups [2d,2e,2f,2g,2h].

The dicationic state of **1** is stable enough for various physicochemical measurements. However, the corresponding dication $\mathbf{1}^{++}$ gradually decomposes in solution at ambient temperature, being far from practical applications such as oligoarylamines-based organic magnetic materials. On the other hand, a tetraaryl-*m*-phenylenediamine (**3**), which has two bromo groups on the central ring, gives an extremely stable dicationic state in solution, revealing no significant decay in solution [3]. Comparing the structure of **3** with that of **1** suggests that the bromo groups play an important role to stabilize the dicationic states.

Previously, we synthesized a series of tetraaryl-*m*-phenylenediamines with bromo groups on the peripheral and/or central rings, revealing from electron transfer stopped-flow (ETSF) measurements that the bromo groups on the central aromatic rings can effectively stabilize the dicationic

---

[*] Corresponding author. Tel.: +81 6 6368 0751; fax: +81 6 6330 3770.
E-mail address: myano@ipcku.kansai-u.ac.jp (M. Yano).

0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.09.059

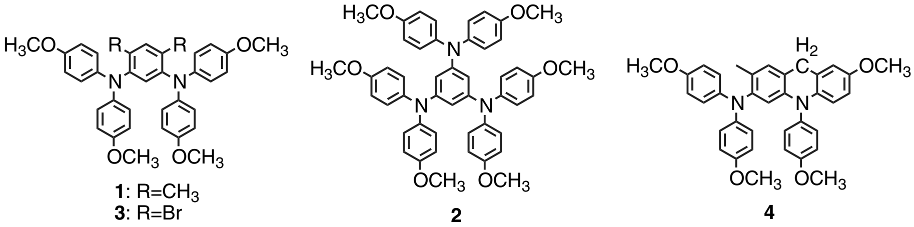

Fig. 1. Structures of compounds **1**–**4**.

states [2k,4]. However, the stabilization mechanism is still not clear. We assumed that the decomposed product was compound **4**, which was generated by intramolecular hydrogen abstraction. Until now, there was no direct evidence for the generation of **4**. Although a number of experimental and theoretical studies have been performed about reaction mechanisms of mono cation radicals [5], triplet dication diradicals have very rarely been dealt with. In this study, we report the generation and decomposition of $\mathbf{1}^{++}$ in preparative scale, and the identification of the structures for the decomposed products.

2. Results and discussion

The diamine **1** was synthesized by the methods reported before [2b]. Compound **3** was synthesized by bromination of *N*,*N*,*N*′,*N*′-tetra(*p*-anisyl)-1,3-phenylenediamine. The synthetic detail of **3** will be reported elsewhere [3]. Fig. 2 shows the NMR spectra of **1** and the corresponding decomposition products. The compound **1** exhibits absorption peaks of the methyl and methoxy groups at 1.97 ppm and 3.75 ppm, respectively (Fig. 2a). The generation of the mono cationic state was conducted as shown below. To the solution of **1** (0.127 g, 0.23 mmol) in dichloromethane (10 ml), 1.5 equiv. of $SbCl_5$ (44.3 µl, 0.35 mmol) in dichloromethane (10 ml) were slowly dropped at 15 °C under nitrogen atmosphere. Upon the addition of $SbCl_5$, the color of the solution immediately turned to blue, indicating the generation of radical species. The solution was stirred for 3 days until no change in solution color was observed. The obtained solution was mixed with aqueous ascorbic acid solution, extracted with chloroform, dried over sodium sulfate, and evaporated under reduced pressure to give pale yellow oil. The NMR spectrum of the product showed approximately quantitative recovery of **1**.

The generation of the dicationic state was conducted similarly. The solution of **1** (0.127 g, 0.23 mmol) in dichloromethane (10 ml) was mixed with 3 equiv. of $SbCl_5$ (87.4 µl, 0.69 mmol) in dichloromethane (10 ml), and allowed to stand for 3 days under the same condition described for the monocation. The color of the solution gradually changed from blue to bluish-purple. The

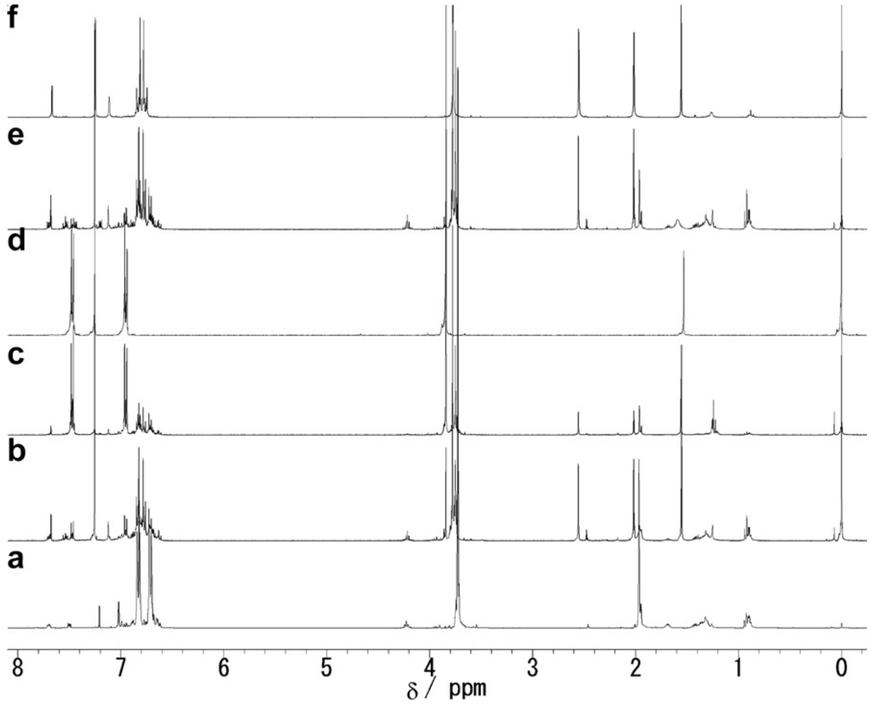

Fig. 2. NMR spectra of **1** and its decomposition products (see the text for details).