

Novel trends of electrochemical oxidation of amino-substituted triphenylamine derivatives

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Abstract

A series of amino-substituted triphenylamine derivatives have been synthesized and the electrochemical and spectral characteristics has been investigated. Triphenylamine is also used as a reference. *p*-Amino-triphenylamine (**1**) showed two reversible redox couples at $E_{1/2} = 0.59$ and 1.09 V in CH_2Cl_2 . The stable cation radical $\mathbf{1}^{\cdot+}$ was generated electrochemically and exhibited strong bands in the visible region as determined in situ by UV/Vis/NIR spectroelectrochemical methods. The second oxidation product $\mathbf{1}^{2+}$ could be generated electrochemically, but was not very stable after long time electrolysis at applied potentials higher than 1.15 V. *p,p'*-Diamino-triphenylamine (**2**), *p*-methyl-*p',p''*-diamino-triphenylamine (**2a**), *p*-methoxy-*p',p''*-diamino-triphenylamine (**2b**) and *p,p',p''*-triamino-triphenylamine (**3**) are more stable in CH_3CN than in CH_2Cl_2 during cyclic scans at oxidation potentials. The oxidation potentials of the various amino-substituted TPA derivatives and the stability of the oxidized products are solvent-dependent and relate to the molecular structures.

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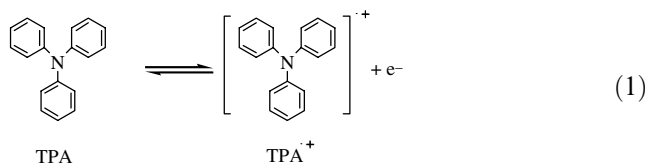
Keywords: Amino-substituted triphenylamine; Electrochemical oxidation; Spectroelectrochemistry; Cation radicals; Dication

1. Introduction

In 1968, Adams and co-workers [1] reported that anodic oxidation of triphenylamine (TPA) leads to TPA cation radical ($\text{TPA}^{\cdot+}$). The stability of the cation radical varies markedly with *para*-substitution. Because of the low ionization potentials, reversible redox behavior and good film-forming properties [2,3], TPA-containing monomers [1,4] and polymers [3] have been synthesized and their charge injection and electroluminescent efficiency have been studied [4–7]. Today, the highly electron-rich TPA derivatives have been chosen

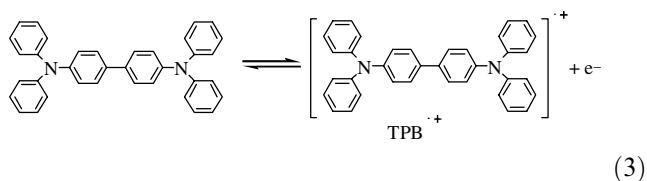
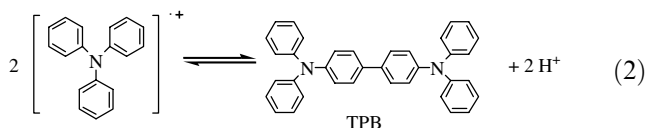
as important candidates for electrical and optical applications such as organic photoconductors, electroluminescence and electrochromic devices [8–10].

The characteristic structure feature of TPA is the nitrogen center, the electroactive site of TPA, which is linked to three electron-rich phenyl groups in a propeller-like geometry [11]. The anodic oxidation pathway of TPA was well reported [1] and is shown in Eqs. (1)–(3). The electrogenerated cation radical $\text{TPA}^{\cdot+}$ dimerized to form tetraphenylbenzidine (TPB), which is more easily oxidized than the TPA molecule.



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The electrochemical properties of TPA are affected when some of the hydrogen atoms are substituted with groups of different electronic strengths [1,4]. It was found that $\text{TPA}^{+\cdot}$ was stabilized when electro-donating groups (methyl, methoxy) were substituted at the *para*-phenyl positions. However, electron-withdrawing groups (nitro, halide) deactivate the cation radical [1]. Nelson and Adams [12] and Vallat and Laviron [13] also reported the effect of *para*-substitution on the rate of benzidine formation. The electro-oxidation of TPA was similar to the anodic oxidation of tertiary aromatic amines, such as *N,N'*-dimethylaniline, where tetramethylbenzidine formation was observed due to the dimerization of the *N,N'*-dimethylaniline cation radical [14]. Recently, kinetic analyses of these short-lived cation radicals have been carried out using ultramicroelectrode voltammetry [15], rapid-scan cyclic voltammetry [16] and electron transfer stopped-flow methods [17].

In 1974, Nelson and co-workers [18] studied the electrochemical oxidation of TPA derivatives, in which all the *para*-phenyl positions were substituted. It was observed that the cation radicals of these derivatives were stable in CH_3CN , and the second electron oxidation was followed by rapid chemical reactions. The carbazoles were obtained with a relatively high yield by the intramolecular cyclization of the dication accompanied by elimination of two protons [18].

In our previous study [4], it was observed that amino groups exhibited quite unique properties in the electrochemistry of TPA. Since amino groups are the most strongly electron-donating groups, their roles in the TPA system are interesting and worthy of investigation. However, little information about multi-amino-substituted TPA can be obtained from the literature. In this continuation study, we aimed to explore the electrochemical and spectral effects of peripheral amino groups on TPA. The intramolecular electron transfer and electronic coupling effects in the oxidized states are also important in the design of new TPA-based polymers for luminescent electronic devices. It is well known that the electrically conductive polymer family of aromatic diamines such as phenylenediamine, benzidine, diamino-anthraquinone and their derivatives have been applied for their multi-functionality [19]. The multi-amino-substituted TPA derivatives are expected to possess novel

characteristics to modify both chemical and physical properties of the aromatic polymers.

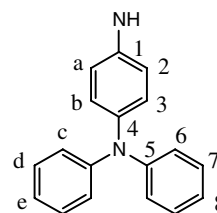
2. Experimental

The chemical structures of the compounds in this study are shown in Fig. 1. TPA was obtained from ACROS. The amino-substituted TPA derivatives were synthesized by reduction of the corresponding nitro-substituted derivatives [4].

2.1. *p*-amino-triphenylamine (I)

(I) was synthesized by Pd/C-catalyzed reduction of the *p*-nitrotriphenylamine obtained from the reaction of diphenylamine with 4-fluoronitrobenzene in the presence of sodium hydride [4]. In a 500-ml round-bottom flask, 20.84 g (0.072 mol) of the desired nitro compound and 0.4 g of Pd/C (10 wt% palladium on activated carbon) were dissolved/suspended in 300 mL of ethanol. The suspension solution was heated to reflux, and 15 mL of hydrazine monohydrate was added dropwise to the mixture, then the solution was stirred at the reflux temperature for 10 h. After cooling to room temperature, the solution was filtered to remove the catalyst, and the solid obtained from the filtrate was recrystallized from ethanol + water under nitrogen to give white needles (15.81 g, yield: 84.6%); m.p. = 148–150 °C measured by differential scanning calorimetry (DSC) at a scan rate of 10 °C/min.

IR (KBr): 3350, 3430 cm^{-1} (N–H stretch). ^1H NMR (DMSO- d_6 , δ , ppm): 6.59 (d, 2H, H_a), 6.90 (d, 4H, H_c), 7.16 (t, 4H, H_d), 6.79 ~ 6.88 (m, 4H, $\text{H}_b + \text{H}_e$), 5.065 (s, 2H, NH). ^{13}C NMR (DMSO- d_6 , δ , ppm): 146.2 (C^1), 115.0 (C^2), 121.0 (C^3), 135.3 (C^4), 147.9 (C^5), 121.4 (C^6), 129.0 (C^7), 128.1 (C^8). Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2$ (260.33): C, 83.04%; H, 6.19%; N, 10.76%. Found: C, 83.35%; H, 6.19%; N, 10.72%.



The other amino-substituted TPA derivatives were obtained and characterized in a similar way. All the chemicals were of analytical grade. Organic solvents were degassed by purging with pre-purified nitrogen gas and dried before use [20]. Tetra-*n*-butylammonium perchlorate (TBAP) was obtained from ACROS and recrystallized twice from ethyl acetate and then dried in vacuo prior to use.

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