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## Synthesis of Oligo(*m*-aniline)

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Abstract: Phenyl-capped dimer, trimer, and tetramer of poly(m-aniline) have been synthesized. Cyclic voltanummetry has proved that the donor ability of these oligomers can be changed according to their length or topology.

In the past few decades, extensive work has been done on the design of high-spin molecules and organic ferromagnets. In particular, the study of oligo(*m*-phenylenecarbene)s,<sup>1</sup> oligo(*m*-phenylene-methyl)s,<sup>2</sup> oligo(*m*-phenylene nitroxide)s,<sup>3</sup> 1,3,5-triaminobenzene cations,<sup>4</sup> *m*-phenylenediacenyl anions,<sup>5</sup> and others<sup>6</sup> has revealed that *m*-phenylene is a promising ferromagnetic coupling unit for the realization of high-spin organic molecules. More importantly, a target of these investigations has been the preparation of polymer-based organic ferromagnets. In this context we have investigated the cation radical form of polyarylamines<sup>7</sup>, especially poly(*m*-aniline) (1),<sup>7b-f</sup> that could have a spin-parallel alignment in the polymer chain being stable compared with high-spin polycarbene.<sup>1</sup> In those organic magnetic polymers, however, the structure-property relationship has not been fully understood. For this reason, we decided to study the synthesis of oligomeric model compounds, which have the advantage of a well-defined structure. Here we report on the preparation of the phenyl-capped dimer, trimer, and tetramer of 1: *N*, *N*'-diphenyl-1,3-phenylenediamine (DP-PDA, **2**), 3,3'-dianilino(diphenylamine) (DA-DPA, **3**), and *N*, *N*'-bis(3-anilinophenyl)-1,3-phenylenediamine (BAP-PDA, **4**), and their donor ability.



Our synthetic strategy is characterized either by (i) one-side-elongation or (ii) both-sides-elongation, both using successive Ullmann condensation reactions. The Ullmann reaction (copper(I) iodide, potassium carbonate, 24 h at  $180^{\circ}$ C) of *m*-bromobenzene and acetanilide, followed by chromatography from ethyl acetate on silica gel, treatment with conc. HCl in ethanol, and then recrystallization from ethanol-water yielded 2 in 23% yield. Unexpectedly, the method reported by Buu-Hoi<sup>8</sup> gave not 2 but 3-hydroxydiphenylamine.



## Scheme 1

Scheme 1 outlines the synthetic route for **3**, corresponding to the one-side-elongation approach. Using the Ullmann reaction, *m*-nitroacetanilide (**5**) was coupled with iodobenzene at  $180^{\circ}$ C overnight under N<sub>2</sub> gas to give acetylated *m*-nitrodiphenylamine (**6**) in 50% yield after column-chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>). Hydrogenation of **6** proceeded quantitatively with Pd on carbon under H<sub>2</sub> gas. After acetylation of **7** (yield 30%), the resultant diamine (**8**) was reacted with *m*-dibromobenzene under N<sub>2</sub> gas for 5 days under the usual conditions of the Ullmann reaction to afford diacetylated N-3-bromophenyl-N'-phenyl-1,3-phenylenediamine (**9**) in 90% yield after filtration (silica gel, ethyl acetate). The double coupled product (**4**) was not obtained in this reaction condition. The third Ullmann reaction with acetanilide (4 days heating under N<sub>2</sub> gas) yielded **10** in 45% yield<sup>9</sup> after working up by filtration through silica gel (eluent: ethyl acetate). The hydrolysis of **10** by the usual method, and then chromatography from ethyl acetate/*n*-hexane (1:1) on silica, finally gave **3** in 63% yield<sup>10</sup> from **10**.

As exhibited in Scheme 2, the synthesis of 4 involves two successive Ullmann reactions based on the both-sides-elongation approach. After Ullmann coupling of 5 and *m*-dibromobenzene (2 days at 180°C), the resultant mixture was column-chromatographed on silica gel (eluent: ethyl acetate/*n*-hexane (9:1)) to afford 11 in 50% yield. Reduction of 11 was achieved by the same procedure as the conversion  $6\rightarrow7$  at 40°C to give 12 in 85% yield. Acetylation of 12 (35% yield) and subsequent treatment with iodobenzene (the second Ullmann reaction, 3 days at 190°C) provided quadracetylated tetramer (14) in 60% yield<sup>9</sup> after repeated chromatography (silica gel, (i) ethyl acetate, (ii) acetone). Eventually, the target tetramer (4) was obtained by refluxing 14 in ethanol containing conc. HCl and by purifying through column-chromatography on silica gel (eluent: ethyl acetate/*n*-hexane (4:1)) in 28% yield<sup>10</sup>.

The electrochemical properties of 2 and 3 were studied by cyclic voltammetry (CV). The cyclic voltammograms of both compounds in *n*-butylnitrile consisted of two- and three-pairs of quasi-reversible waves



## Scheme 2

corresponding to the number of nitrogen atoms. The observed quasi-reversibility was not improved by cooling the CV cell in contrast to the tertiary arylamines.<sup>4c,d</sup> Interestingly enough, the  $E_1$  value of **3** is lower by 0.23 V than that of **2**, as shown in Table 1, indicating that the donor ability is enhanced by elongating the length of the oligomers. In comparison with N, N', N''-triphenyl-1,3,5-triaminobenzene (15)<sup>8</sup>, the isomer of **3**, **3** has low oxidation potentials, in particular  $E_3$ , probably because in **15** the oxidized moieties are concentrated in the

Table 1. Oxidation Potentials  $(V^{-1})^{a}$  of 2, 3, and 15 in *n*-Butyronitrile Containing 0.1M TBABF<sub>4</sub> at -50°C.<sup>b</sup>

	Compounds	E <sub>1</sub>	E <sub>2</sub>	E <sub>3</sub>	<del></del>
2	0,0,0	+0.95	+1.20		
3	0,0,0,0	+0.72	+0.95	+1.28	
15		+0.96	+1.56	+2.18	

\* Potentials vs. Ag wire quasi-reference electrode.

<sup>b</sup> Oxidation potentials correspond to the anodic peak potentials of the quasi-reversible oxidation peaks found in cyclic voltammograms performed at a Pt electrode and at a scan rate 200 mVs<sup>-1</sup>.

central phenyl ring. We are now trying to prepare the charge-transfer salts of these oligomers with inorganic acceptors.

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- 9. Compounds 10 and 14 gave satisfactory elemental analysis results.
- Spectral data for 3 and 4. 3: <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 5.65 (s br, 3H), 6.6-7.3 (m, 18H); 13C NMR (67.5 MHz, CDCl<sub>3</sub>) δ 106.81, 110.37, 110.69, 118.27, 121.12, 129.31, 130.11, 142.90, 144.10, 144.33; HRMS calcd. for C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>: 351.1734, found 351.1739. 4: <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 5.65 (s br, 4H), 6.6-7.3 (m, 22H); <sup>1</sup>3C NMR (67.5 MHz, CDCl<sub>3</sub>) δ 106.84, 107.25, 110.26, 110.64, 110.75, 118.31, 121.12, 129.30, 130.06, 130.09 142.90, 144.06, 144.10, 144.35; HRMS calcd. for C<sub>30</sub>H<sub>26</sub>N<sub>4</sub>: 442.2156, found 442.2165.

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