

# Synthesis and spectroscopic properties of aniline tetramers. Comparative studies

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A new synthetic method involving  $S_NAr$  coupling of 4-fluoronitrobenzene to arylamines, followed by the reduction of the nitro groups, has been developed. Two types of aniline oligomers, namely  $Ph/NH_2$  and  $NH_2/NH_2$  tetramers have been prepared by this method. Tetramers in the leucoemeraldine and in the emeraldine oxidation states were characterized by NMR, UV-Vis-NIR, IR and mass spectroscopies. It shown that the  $NH_2/NH_2$  tetramer oxidized to the emeraldine state forms two isomers: syn and anti. The oxidation of the  $Ph/NH_2$  tetramer leads to the creation of positional isomers, depending on the synthetic method.

## Introduction

Oligoanilines can be considered as good model compounds of polyaniline, the most technologically important conducting polymer. Studies of the topological and geometrical isomers formed after oxidation of amines allow one to understand the complexity of the molecular interactions in polyaniline. The most interesting form of polyaniline is emeraldine, which contains *ca.* 50% amine and *ca.* 50% imine groups, that is one of 4 rings is quinoid, the remaining three being benzoid. For this reason the shortest model compound for emeraldine must comprise four aniline repeat units. Many synthetic methods involving different types of condensation reactions have been reported as suitable for the synthesis of phenyl/ $NH_2$  and phenyl/phenyl end-capped tetramers. Honzl and Tlustakova<sup>1</sup> obtained the tetramer by the condensation of *N*-phenyl-1,4-phenylenediamine with diethyl succinoylsuccinate, followed by hydrolysis, decarboxylation and aromatization. The condensation of *p*-phenylenediamine with *p*-anilinophenol was reported by Ochi *et al.*<sup>2</sup> An Ullmann-type coupling reaction between acetanilides and 4-iodonitrobenzene was used by Rebourt *et al.*<sup>3</sup> The tetramer was obtained by reduction and deacetylation reactions but no detailed experimental procedure was given. The phenyl/ $NH_2$  end-capped tetramer was prepared by oxidative coupling of *N*-phenyl-1,4-phenylenediamine in the presence of  $FeCl_3 \cdot 6H_2O$  as an oxidant by Zhang *et al.*<sup>4</sup> The phenyl/phenyl end-capped tetramer was synthesized by Wei *et al.*<sup>5</sup> using *p*-phenylenediamine, diphenylamine and  $(NH_4)_2S_2O_8$  as a suitable oxidizing agent. Recently, Wang and MacDiarmid<sup>6</sup> have reported the synthesis of a phenyl/phenyl end-capped tetramer by the condensation of *N*-phenyl-1,4-phenylenediamine with hydroquinone in the presence of titanium *n*-butoxide. A general and elegant way to prepare different types of oligoanilines was proposed by Sadighi *et al.*<sup>7</sup> who synthesized oligomers by palladium catalyzed amination of aryl halides, followed by deprotection of the amine groups. However, it should be noted that the most popular method for the preparation of aniline tetramers is still oxidative coupling, due to its simplicity.

The present study reports a simple method for the synthesis of phenyl/ $NH_2$  ( $Ph/NH_2$ ) and  $NH_2/NH_2$  end-capped aniline tetramers by the  $S_NAr$  reaction of 4-fluoronitrobenzene with the corresponding aromatic amines. The coupling is followed by reduction of the nitro groups to arylamines. The iterative

coupling/reduction sequence allows to prepare tetramers of both the above-mentioned types. Moreover, the  $S_NAr$  reaction is carried out in mild conditions and therefore protection of the amine groups is unnecessary. The obtained tetramers in both the reduced and oxidized forms are characterized by elemental analyses, mass spectroscopy, NMR, IR and UV-Vis-NIR spectroscopies. The spectroscopic properties of such oligomers are compared with the properties of the  $Ph/NH_2$  tetramer obtained by oxidative coupling.

$Ph/NH_2$  and  $Ph/Ph$  end-capped tetramers contain 4 nitrogen atoms but different numbers of phenyl rings (4 and 5, respectively). The conjugation length (or the length of the peripheral bonds) is different in both cases, therefore the properties of these compounds cannot be easily compared. In our study the name “tetramer” is used to denote compounds that contain 4 phenyl rings and 4 (in the case of  $Ph/NH_2$ ) or 5 (in the case of  $NH_2/NH_2$ ) nitrogen atoms.

## Experimental

### Materials and methods

All compounds studied were subjected to elemental analyses. C, H and N were determined by combustion analysis.

<sup>1</sup>H NMR spectra were recorded on a Varian Mercury 400 MHz and referenced with respect to TMS. IR spectra were recorded on a Bio-RAD FTS-165 using KBr pellets. UV-Vis-NIR spectra were registered using a Lambda 2 (Perkin-Elmer) spectrometer in the spectral range of 200–1100 nm. Mass spectra were measured using the electron impact ionization method on an AMD 604 instrument.

*N*-Phenyl-1,4-phenylenediamine, 4,4'-diaminodiphenylamine sulfate, triethylamine, dimethyl sulfoxide (DMSO), 4-fluoronitrobenzene,  $FeCl_3$ , ammonium persulfate, Sn powder and hydrazine monohydrate were purchased from Aldrich Chemical Co. Acetone, dichloromethane, ethyl acetate, sodium pyrosulfite, HCl, KOH, NaOH were purchased from POCh (Poland). *N*-Phenyl-1,4-phenylenediamine was crystallized from water and dried over KOH in a vacuum desiccator. Triethylamine was dried over KOH. DMSO was stored over thermally activated 4 Å molecular sieves. 4-Fluoronitrobenzene, Sn powder, the oxidants and the solvents were used as supplied.

## Syntheses

**4,4'-Diaminodiphenylamine 1.** 4,4'-Diaminodiphenylamine sulfate (*ca.* 1.2 g) was dissolved in 50 ml of 1 wt % KOH solution. Sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ; 0.6 g) was added to the solution and the mixture was boiled for 15 min, then filtered and crystallized. The white crystals were dried over KOH in a vacuum desiccator. M.p. 158–160 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  6.76 (s, 1H), 6.63 (s, 4H), 6.45 (m, 4H), 4.46 (s, 4H). IR ( $\text{cm}^{-1}$ ) 3409, 3390, 3034, 1612, 1515, 1312, 1275, 823. Anal. calcd for  $\text{C}_{12}\text{H}_{13}\text{N}_3$ : C, 72.36; H, 6.53; N, 21.11; found: C, 69.68; H, 6.50; N, 20.39.

**Tetramer  $\text{NO}_2/\text{NO}_2$  2.** 4,4'-Diaminodiphenylamine (1; 0.995 g, 5 mmol) and 4-fluoronitrobenzene (1.41 g, 10 mmol) were dissolved in 15 ml of DMSO. Triethylamine (1.7 ml, 12 mmol) was added to the solution and the mixture was stirred and heated at 90 °C for 3 days under argon atmosphere to avoid oxidation of the amine. Then the solution was allowed to cool to room temperature and poured into 200 ml of distilled water. The brown-orange solid was precipitated, washed several times with distilled water and dried in air. The crude product was purified by liquid chromatography (silica gel, acetone– $\text{CH}_2\text{Cl}_2$  1:4). The powder was recrystallized from methanol as orange-brown crystals (0.992 g, 45% yield after recrystallization). M.p. 184–186 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  9.12 (s, 2H), 8.22 (s, 1H), 8.05–8.03 (m, 4H), 7.15–7.09 (m, 8H), 6.91–6.89 (m, 4H). IR ( $\text{cm}^{-1}$ ) 3355, 1602, 1523, 1498, 1299, 1114, 830. Anal. calcd for  $\text{C}_{24}\text{H}_{19}\text{N}_5\text{O}_4$ : C, 65.31; H, 4.31; N, 15.87; found: C, 64.02; H, 4.19; N, 15.45.

**Tetramer  $\text{NH}_2/\text{NH}_2$  3.** Tetramer  $\text{NO}_2/\text{NO}_2$  (2; 0.8 g, 1.81 mmol) was stirred with 4 ml of 37% HCl under argon atmosphere for 15 min at room temperature. Tin powder (3.44 g, 29.0 mmol) and 37% HCl (20 ml) were added in portions and the mixture was refluxed for *ca.* 3 h until a whitish yellow precipitate was formed. After cooling to room temperature 10 ml of 20 wt % NaOH solution and then NaOH granules were slowly added with constant stirring. The pH of the mixture was adjusted to 12. The white precipitate was filtered under argon atmosphere and the product was washed several times with 20 wt % NaOH solution, then with distilled water to pH = 7. The whitish gray powder was dried over KOH in a vacuum desiccator (0.18 g, 75% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.21 (s, 1H), 7.08 (s, 2H), 6.79–6.77 (m, 4H), 6.73–6.71 (m, 8H), 6.48–6.46 (m, 4H), 4.60 (s, 4H). IR ( $\text{cm}^{-1}$ ) 3387, 3345, 3022, 1609, 1511, 1303, 1263, 1223, 817. Anal. calcd for  $(\text{C}_{24}\text{H}_{23}\text{N}_5)(\text{H}_2\text{O})_{0.7}$ : C, 73.77; H, 6.25; N, 17.93; found: C, 74.21; H, 6.24; N, 17.99. EI-MS:  $m/z$  = 381.7  $[\text{M}]^+$ .

**Tetramer  $\text{NH}_2/\text{NH}_2$ -EB 4.** Tetramer  $\text{NH}_2/\text{NH}_2$  was oxidized to the emeraldine oxidation state by the following procedure. 3 (0.378 g, 0.99 mmol) was suspended in 10 ml of 0.1 M HCl aqueous solution with constant stirring for 30 min at 0 °C. Ammonium persulfate (0.226 g, 0.99 mmol) was dissolved in 10 ml of 0.1 M HCl and cooled to 0 °C. The oxidant solution was added dropwise to the tetramer suspension with strong stirring. The color of the suspension changed to dark green. The reaction was carried out for 3 h at 0 °C. The very fine suspension was coagulated in distilled water and then filtered. The green precipitate was washed several times with distilled water and was deprotonated in 30 ml of 0.1 M  $\text{NH}_3$  aqueous solution for 16 h at room temperature. The color turned to blue. The precipitate was filtered, washed with distilled water and dried over KOH.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.86/7.85 (s, 1H), 7.06/7.04 (m, 1H), 6.96/6.95 (s, 2H), 6.94–6.91 (m, 1H), 6.89–6.83 (m, 6H), 6.79–6.76 (m, 2H), 6.61–6.59 (m, 2H), 6.56–6.54 (m, 2H), 5.44/5.43 (s, 2H), 4.83 (s, 2H). IR ( $\text{cm}^{-1}$ ) 3390, 3270, 3032, 1599, 1501, 1380, 1317, 1286, 1267, 1167, 832. Anal. calcd for  $(\text{C}_{24}\text{H}_{21}\text{N}_5)(\text{H}_2\text{O})_{0.4}$ : C,

74.57; H, 5.64; N, 18.12; found: C, 73.63; H, 5.44; N, 17.50. EI-MS:  $m/z$  = 380.3  $[\text{M} + \text{H}]^+$ .

**Trimer Ph/ $\text{NO}_2$  5.** *N*-Phenyl-1,4-phenylenediamine (1.106 g, 6 mmol) and 4-fluoronitrobenzene (0.846 g, 6 mmol) were dissolved in 15 ml of DMSO. Triethylamine (0.85 ml, 6 mmol) was added to the solution and then the mixture was stirred and heated at 90 °C for 5 days under argon atmosphere. The procedure was the same as for the preparation of tetramer  $\text{NO}_2/\text{NO}_2$  2, except that the purification by chromatography was done with 1:4 ethyl acetate– $\text{CH}_2\text{Cl}_2$ . The product was recrystallized from methanol as a red powder (0.85 g, 46.5% yield). M.p. 132–134 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  9.12 (s, 1H), 8.17 (s, 1H), 8.05–8.03 (m, 2H), 7.21 (t, 2H), 7.12–7.11 (m, 4H), 7.06–7.04 (m, 2H), 6.91–6.89 (m, 2H), 6.79 (t, 1H). IR ( $\text{cm}^{-1}$ ) 3380, 3030, 1595, 1520, 1494, 1463, 1319, 1286, 1259, 1185, 1110, 833, 795, 695. Anal. calcd for  $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_2$ : C, 70.82; H, 4.92; N, 13.77; found: C, 70.42; H, 5.04; N, 13.91.

**Trimer Ph/ $\text{NH}_2$  6.** Trimer Ph/ $\text{NO}_2$  5 was reduced to trimer Ph/ $\text{NH}_2$  6 in exactly the same manner as described for the reduction of tetramer  $\text{NO}_2/\text{NO}_2$  2. Trimer Ph/ $\text{NO}_2$  (5; 0.505 g, 1.65 mmol) was reduced with Sn powder (1.57 g, 13.2 mmol) and 20 ml of 37% HCl. The amine formed was completely soluble in HCl. After neutralization the white powder was precipitated (0.327 g, 72% yield). M.p. 152–155 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.65 (s, 1H), 7.27 (s, 1H), 7.10 (t, 2H), 6.91–6.89 (m, 2H), 6.84–6.82 (m, 2H), 6.79–6.76 (m, 4H), 6.62 (t, 1H), 6.51–6.49 (m, 2H), 4.72 (s, 2H). IR ( $\text{cm}^{-1}$ ) 3435, 3370, 3025, 1601, 1526, 1513, 1496, 1311, 1259, 1224, 1172, 821, 746, 697. Anal. calcd for  $(\text{C}_{18}\text{H}_{17}\text{N}_3)(\text{H}_2\text{O})_{0.5}$ : C, 76.05; H, 6.34; N, 14.79; found: C, 74.26; H, 5.95; N, 14.45. EI-MS:  $m/z$  = 275.5  $[\text{M}]^+$ .

**Tetramer Ph/ $\text{NO}_2$  7.** Tetramer Ph/ $\text{NO}_2$  (7) was prepared in the same manner as trimer Ph/ $\text{NO}_2$  5. Trimer Ph/ $\text{NH}_2$  (6; 0.65 g, 2.4 mmol), 4-fluoronitrobenzene (0.338 g, 2.4 mmol) and triethylamine (0.35 ml, 2.4 mmol) were dissolved in 10 ml of DMSO. The mixture was heated at 90 °C for 3 days under argon atmosphere. The crude product was purified by chromatography (silica gel, ethyl acetate– $\text{CH}_2\text{Cl}_2$  1:4), then recrystallized from methanol (0.44 g, 46% yield). M.p. 175–178 °C.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  9.07 (s, 1H), 8.04–8.01 (m, 2H), 7.95 (s, 1H), 7.88 (s, 1H), 7.16 (t, 2H), 7.09–7.07 (m, 2H), 7.03–7.00 (m, 6H), 6.95–6.94 (m, 2H), 6.87–6.85 (m, 2H), 6.70 (t, 1H). IR ( $\text{cm}^{-1}$ ) 3391, 3311, 3034, 1595, 1524, 1509, 1287, 1223, 1188, 1110, 824, 748, 695. Anal. calcd for  $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_2$ : C, 72.73; H, 5.05; N, 14.14; found: C, 72.05; H, 4.61; N, 14.01.

**Tetramer Ph/ $\text{NH}_2$  8.** Tetramer Ph/ $\text{NO}_2$  (7; 0.95 g, 2.4 mmol) was reduced with Sn powder (2.3 g, 19.2 mmol) and 20 ml of 37% HCl as described above. The obtained white powder was dried over KOH in a vacuum desiccator (0.64 g, 73% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.70 (s, 1H), 7.45 (s, 1H), 7.17 (s, 1H), 7.11 (t, 2H), 6.95–6.93 (m, 2H), 6.87–6.84 (m, 6H), 6.77–6.75 (m, 4H), 6.64 (t, 1H), 6.51–6.48 (m, 2H), 4.63 (s, 2H). IR ( $\text{cm}^{-1}$ ) 3389, 3021, 1598, 1527, 1513, 1495, 1304, 1264, 1220, 817, 747, 693. Anal. calcd for  $\text{C}_{24}\text{H}_{22}\text{N}_4$ : C, 78.69; H, 6.01; N, 15.30; found: C, 75.09; H, 5.68; N, 14.27. EI-MS:  $m/z$  = 366.7  $[\text{M}]^+$ .

**Tetramer Ph/ $\text{NH}_2$ -EB 9.** Tetramer Ph/ $\text{NH}_2$  8 was oxidized to the emeraldine oxidation state exactly in the same manner as tetramer  $\text{NH}_2/\text{NH}_2$  3 (see above).  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ )  $\delta$  8.36, 7.68, 7.24, 7.12, 6.93–6.86, 6.69–6.64, 6.50, 5.49, 4.73. Anal. calcd for  $(\text{C}_{24}\text{H}_{20}\text{N}_4)(\text{H}_2\text{O})_1$ : C, 75.39; H, 5.76; N, 14.66; found: C, 70.62; H, 5.32; N, 13.64.

**Tetramer Ph/NH<sub>2</sub>-EB(MD) 10.** Tetramer Ph/NH<sub>2</sub> **10** in the oxidation state of emeraldine was synthesized according to the method of Zhang *et al.*<sup>4</sup> <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 8.38 (s, 1H), 7.24 (t, 2H), 7.09 (s, 4H), 7.03–6.96 (m, 5H), 6.91–6.80 (m, 2H), 6.82–6.79 (m, 2H), 6.61–6.60 (m, 2H), 5.53 (s, 2H). IR (cm<sup>-1</sup>) 3377, 3204, 3028, 1596, 1513, 1496, 1324, 1168, 842, 744, 693. Anal. calcd for (C<sub>24</sub>H<sub>20</sub>N<sub>4</sub>)·(H<sub>2</sub>O)<sub>0.5</sub>: C, 77.21; H, 5.63; N, 15.01; found: C, 77.58; H, 5.58; N, 14.88. EI-MS: *m/z* = 365.3 [M + H]<sup>+</sup>.

**Tetramer Ph/NH<sub>2</sub>(MD) 11.** Tetramer Ph/NH<sub>2</sub>-EB(MD) **10** was reduced to the leucoemeraldine form according to the procedure of Wei *et al.*<sup>8</sup> Tetramer **10** (0.1 g, 2.7 mmol) was suspended and refluxed in hydrazine monohydrate (30 mL, 0.62 mol) under argon atmosphere for 24 h. The whitish gray powder was dried in vacuum. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 7.69 (s, 1H), 7.45 (s, 1H), 7.17 (s, 1H), 7.11 (t, 2H), 6.94–6.92 (m, 2H), 6.87–6.83 (m, 6H), 6.76–6.74 (m, 4H), 6.64 (t, 1H), 6.50–6.48 (m, 2H), 4.63 (s, 2H). IR (cm<sup>-1</sup>) 3390, 3921, 1600, 1529, 1510, 1498, 1308, 1220, 817, 745, 695. Anal. calcd for C<sub>24</sub>H<sub>22</sub>N<sub>4</sub>: C, 78.69; H, 6.01; N, 15.30; found: C, 77.19; H, 5.81; N, 14.99. EI-MS: *m/z* = 366.3 [M]<sup>+</sup>.

## Results and discussion

It is widely known that diarylamines are formed by the reaction of activated fluoroarens with arylamines in dipolar aprotic solvents. We have chosen this type of reaction for the preparation of phenyl/NH<sub>2</sub> and NH<sub>2</sub>/NH<sub>2</sub> end-capped tetramers of aniline. In the presence of a base the reaction of arylamines with 4-fluoronitrobenzene results in the formation of arylnitroamines (see Scheme 1).

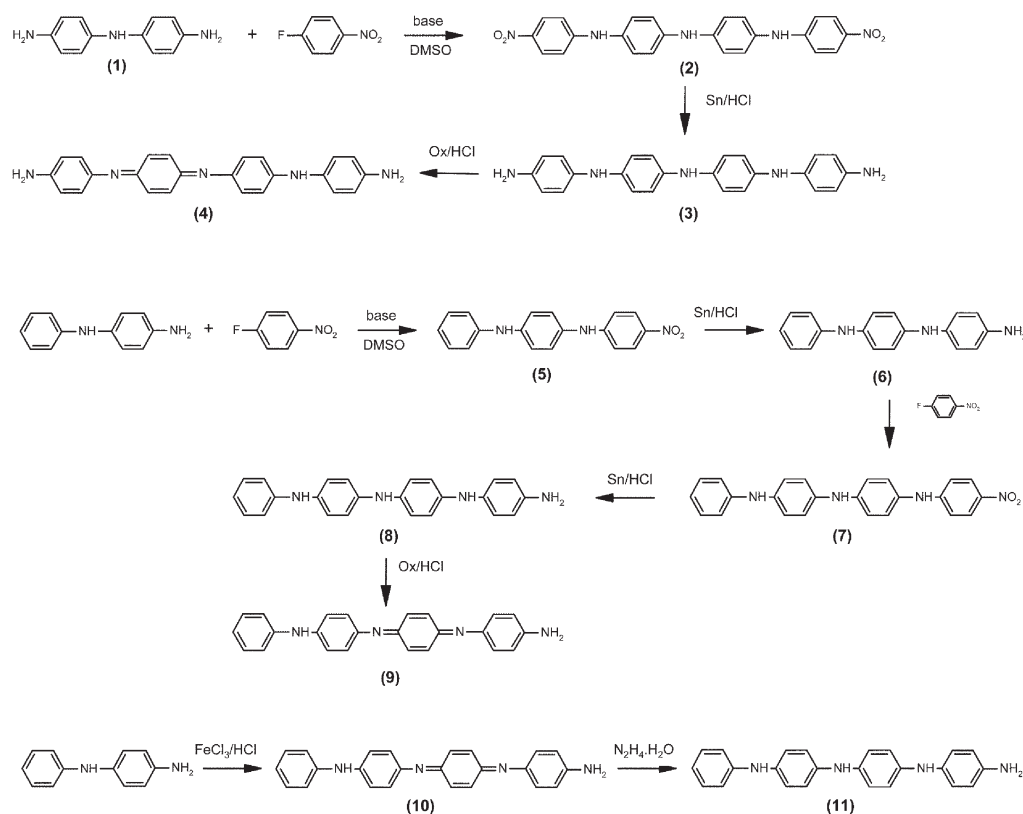
Monodirectional or bidirectional growth of the chain length is possible by using unsymmetrical or symmetrical arylamines. We found that in the presence of K<sub>2</sub>CO<sub>3</sub> or KF, agents frequently used for this type of reaction,<sup>8,9</sup> branched amines

(triarylamines) are preferentially formed even with an excess of amines and at low temperature (50 °C). However, the use of triethylamine as a base ensures the formation of linear arylnitroamines. In this case the reaction fulfils the normal criterion for an S<sub>N</sub>Ar reaction. As compared to the previously reported Ullmann-type coupling,<sup>3</sup> the present method does not require protection of the amine groups and proceeds at a relatively low temperature (90 °C). Compound **2** (tetramer NO<sub>2</sub>/NO<sub>2</sub>) was reduced directly to the tetramer NH<sub>2</sub>/NH<sub>2</sub> **3**. Tetramer Ph/NH<sub>2</sub> **8** was obtained by an iterative coupling/reduction sequence.

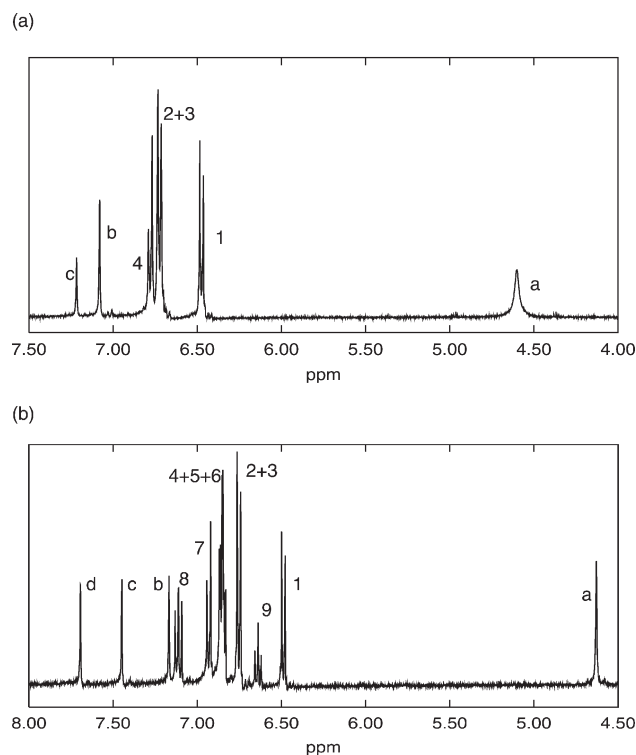
Tetramer Ph/NH<sub>2</sub>-EB(MD) **10** was also prepared by the oxidative coupling method of Zhang *et al.*<sup>4</sup> The spectroscopic properties of these three tetramers in the leucoemeraldine and the emeraldine oxidation states have been studied. The synthetic routes used to obtain the different types of tetramers are presented in Scheme 1.

In Fig. 1 the <sup>1</sup>H NMR solution spectra of tetramers NH<sub>2</sub>/NH<sub>2</sub> [**3**, Fig. 1(a)] and Ph/NH<sub>2</sub> [**8**, Fig. 1(b)] in the leucoemeraldine state are presented. The spectra of the Ph/NH<sub>2</sub> tetramers, obtained either by the S<sub>N</sub>Ar coupling/reduction sequence **8** or *via* the oxidative coupling/reduction method **11**, were exactly the same. Magnetically inequivalent protons are indicated in Scheme 2.

The signals of terminal NH<sub>2</sub> group protons appear at 4.60 and 4.63 ppm in the spectra of NH<sub>2</sub>/NH<sub>2</sub> **3** and Ph/NH<sub>2</sub> (**8** or **11**) tetramers, respectively. The positions of the other –NH– signals are influenced by the number of electron-donating amine groups and by the character of the neighboring aromatic rings. Thus, the signal at 7.08 ppm can be attributed to –NH<sub>b</sub>– and that at 7.21 ppm to –NH<sub>c</sub>– protons in the spectrum of NH<sub>2</sub>/NH<sub>2</sub> tetramer **3**. The positions of the –NH<sub>b</sub>– and –NH<sub>c</sub>– signals are displaced to 7.17 and 7.45 ppm in the spectrum of Ph/NH<sub>2</sub> tetramer **8**. The peak related to the –NH<sub>d</sub>– proton is located at 7.70 ppm. The greater nucleophilic character of the NH<sub>2</sub>/NH<sub>2</sub> tetramer as compared to the Ph/NH<sub>2</sub> one is also evidenced in the position of the aromatic



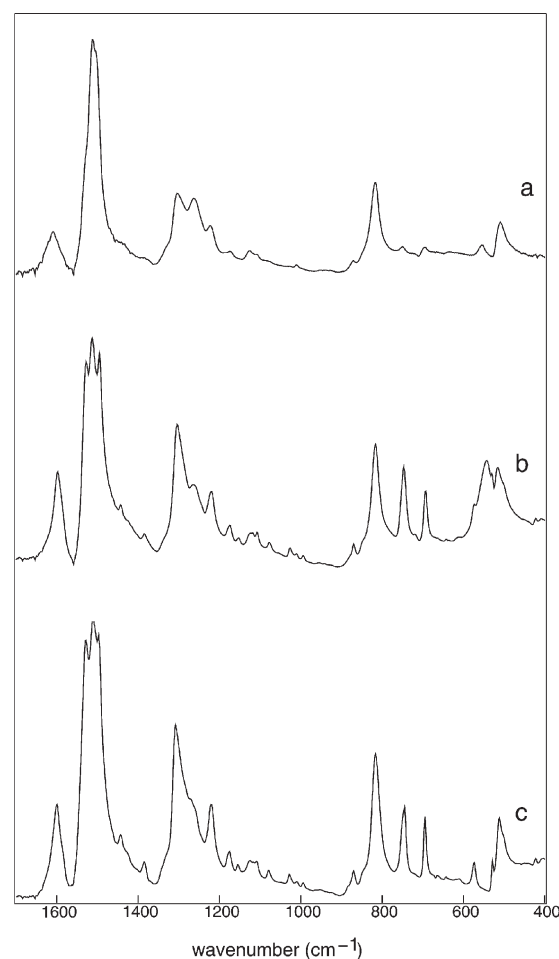
**Scheme 1** The syntheses of Ph/NH<sub>2</sub> and NH<sub>2</sub>/NH<sub>2</sub> tetramers in the leucoemeraldine and emeraldine oxidation states.



**Fig. 1** The  $^1\text{H}$  NMR spectra in  $\text{DMSO-d}_6$  solution of (a)  $\text{NH}_2/\text{NH}_2$  tetramer **3**, (b)  $\text{Ph}/\text{NH}_2$  tetramer **8** in the leucoemeraldine oxidation state.

proton signals. These appear at lower  $\delta$  values in the spectrum of the  $\text{NH}_2/\text{NH}_2$  tetramer **3** as compared to those characteristic of  $\text{Ph}/\text{NH}_2$  tetraamine **8**. It should be noted that both types of molecules correspond to  $\text{AA}'\text{BB}'$  systems. Therefore, for aromatic proton signals we do not observe simple doublets but multiplets. In the spectrum of  $\text{NH}_2/\text{NH}_2$  tetramer **3** the multiplets at 6.48–6.46, 6.73–6.71, 6.79–6.77 ppm can be attributed to the  $\text{H}_1$ ,  $\text{H}_2 + \text{H}_3$ ,  $\text{H}_4$  protons, respectively. In the spectrum of the  $\text{Ph}/\text{NH}_2$  tetramer **8** the signals appear at 6.50–6.48 ( $\text{H}_1$ ), 6.76–6.74 ( $\text{H}_2$  and  $\text{H}_3$ ), 6.87–6.83 ( $\text{H}_4$ ,  $\text{H}_5$ ,  $\text{H}_6$ ), 6.94–6.92 ( $\text{H}_7$ ) ppm. The appearance of two triplets at 7.11 ( $\text{H}_8$ ) and 6.64 ( $\text{H}_9$ ) ppm confirms the presence of the terminal phenyl ring in the  $\text{Ph}/\text{NH}_2$  tetramer **8**. The observed  $^1\text{H}$  NMR spectra agree with the postulated formula of the synthesized tetramers. Moreover, the last method results in the formation of a tetramer coupled only in the para position.

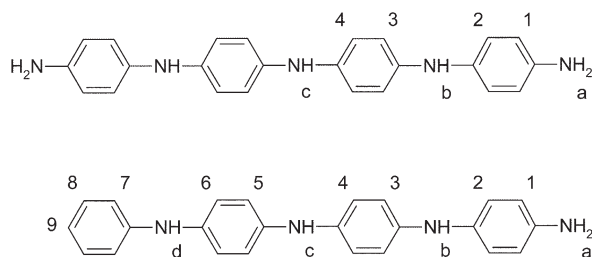
In Fig. 2 the IR spectra of the three tetramers **3**, **8** and **11** are shown. They exhibit features typical of the reduced form, that is the leucoemeraldine oxidation state. The bands originating from N–H or  $\text{NH}_2$  stretching vibrations can be distinguished at 3390  $\text{cm}^{-1}$  for  $\text{Ph}/\text{NH}_2$  tetramers **8** and **11** and at 3387  $\text{cm}^{-1}$  with a shoulder at 3345  $\text{cm}^{-1}$  for  $\text{NH}_2/\text{NH}_2$  tetramer **3**. The modes due to a combination of C–H bending and CC



**Fig. 2** IR spectra of (a)  $\text{NH}_2/\text{NH}_2$  tetramer **3**, (b)  $\text{Ph}/\text{NH}_2$  tetramer **8**, (c)  $\text{Ph}/\text{NH}_2(\text{MD})$  tetramer **11**.

stretching vibrations appear at 1528, 1513 and 1495  $\text{cm}^{-1}$  in the spectra of  $\text{Ph}/\text{NH}_2$  tetramers and at 1511  $\text{cm}^{-1}$  with a shoulder at 1495  $\text{cm}^{-1}$  in the spectrum of  $\text{NH}_2/\text{NH}_2$  tetraamine **3**. Similar modes were observed by Boyer *et al.*<sup>10</sup> for  $\text{Ph}/\text{NH}_2$  oligomers. The comparison of the bands located in this region suggests that the peak at 1528  $\text{cm}^{-1}$  can be assigned to the vibration of the terminal phenyl ring of the  $\text{Ph}/\text{NH}_2$  tetramer (**8** or **11**), because it is absent in the spectrum of 4,4'-diaminodiphenylamine (not presented in Fig. 2) as well as in the spectrum of the  $\text{NH}_2/\text{NH}_2$  tetramer **3**. There are some differences in the interpretation of the nature of the peaks located at 1303 and 1264  $\text{cm}^{-1}$ . Choi and Kertesz<sup>11</sup> proposed that the mode at 1303  $\text{cm}^{-1}$  is due to C–N stretching in the  $C_i$  point group whereas Quillard *et al.*<sup>12</sup> suggested that the C–N stretching can be related to the peak at 1264  $\text{cm}^{-1}$ . Comparing the intensities of the peaks shown in the spectra of the tetramers we are inclined to follow the interpretation given by Quillard *et al.* Moreover, the peaks attributed to the C–H out-of-plane deformation of 1,4-disubstituted rings at 816  $\text{cm}^{-1}$  and mono-substituted rings at 746 and 695  $\text{cm}^{-1}$  appear in the spectra of  $\text{Ph}/\text{NH}_2$  tetramers **8** and **11** whereas only the peak at 817  $\text{cm}^{-1}$  is present in the  $\text{NH}_2/\text{NH}_2$  tetramer **3** spectrum.

Tetramers  $\text{Ph}/\text{NH}_2$  **8** and  $\text{NH}_2/\text{NH}_2$  **3** synthesized by the  $\text{S}_{\text{N}}\text{Ar}$  coupling/reduction sequence were oxidized to the emeraldine form using ammonium persulfate in a 0.1 M HCl solution. This oxidation can be conveniently followed by UV-Vis-NIR spectroscopy. In the reduced state for both  $\text{NH}_2/\text{NH}_2$  **3** and  $\text{Ph}/\text{NH}_2$  **8** tetramers only one peak is observed, at 325 and 322 nm, respectively, ascribed to the  $\pi$ – $\pi^*$  transition in the aromatic ring. The oxidation process gives rise to new peaks in the less energetic region of the spectrum



**Scheme 2** Two types of tetramers:  $\text{NH}_2/\text{NH}_2$  **3** and  $\text{Ph}/\text{NH}_2$  (**8** or **11**) end-capped tetraamines.



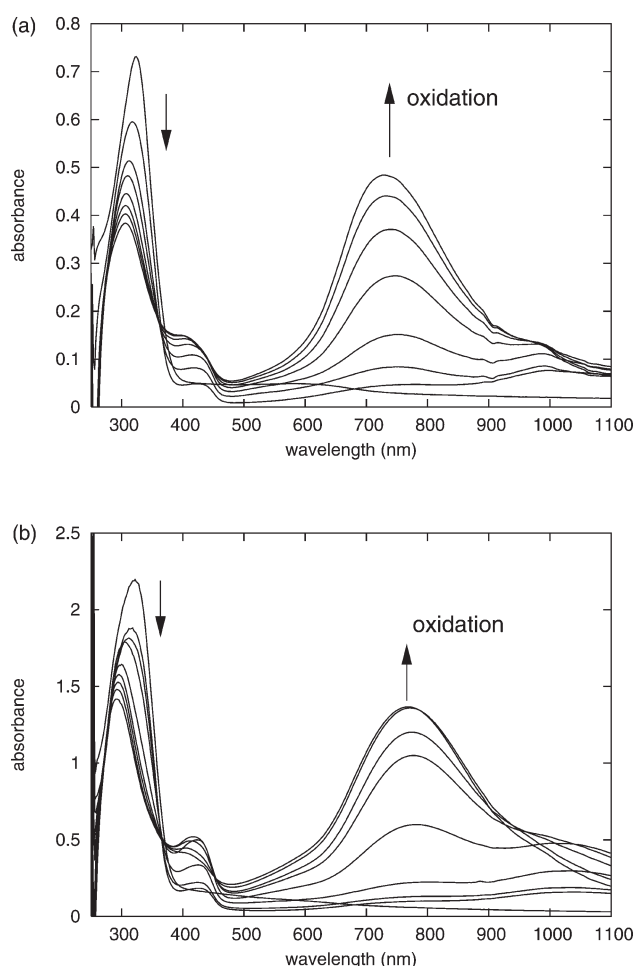
(Fig. 3). In particular, for  $\text{NH}_2/\text{NH}_2$  tetramer **3**, in the first step of the oxidation two new peaks appear at 426 and *ca.* 1000 nm. Further oxidation causes a hypsochromic shift in the position of all peaks present in the spectrum and the appearance of a new peak at *ca.* 750 nm, which dominates the spectrum at the end of the oxidation process. Thus, the oxidized tetramer can be characterized by the following absorption bands: 306, 410 and 730 nm. The behavior of the  $\text{Ph}/\text{NH}_2$  tetramer **8** is similar [(Fig. 3(b))]. The most important feature observed in the oxidation induced spectra of  $\text{NH}_2/\text{NH}_2$  **3** and  $\text{Ph}/\text{NH}_2$  **8** consists in the fact that the band in the vicinity of 1000 nm appears in the initial stages of the oxidation and vanishes as the oxidation proceeds. It should be noted that the spectra of the oxidized tetramers are characteristic of their protonated forms, which is not unexpected because the oxidation reaction is carried out in an acidic medium.

After deprotonation the absorption spectrum (not shown) of oxidized  $\text{NH}_2/\text{NH}_2$  tetramer **4** shows peaks at 320 nm, which can be attributed to a  $\pi\text{-}\pi^*$  transition, and at 608 nm ascribed to an exciton transition in the quinoid ring. In the spectrum of deprotonated, oxidized  $\text{Ph}/\text{NH}_2$  tetramer **9** the maxima are located at 306 and 588 nm in DMSO solution and at 290 and 550 nm in  $\text{CHCl}_3$  solution. The positions of these peaks are in excellent agreement with the location of the peaks observed in the spectrum of  $\text{Ph}/\text{NH}_2\text{-EB(MD)}$  tetramer **10** and agrees with the data published by MacDiarmid *et al.*<sup>13</sup>

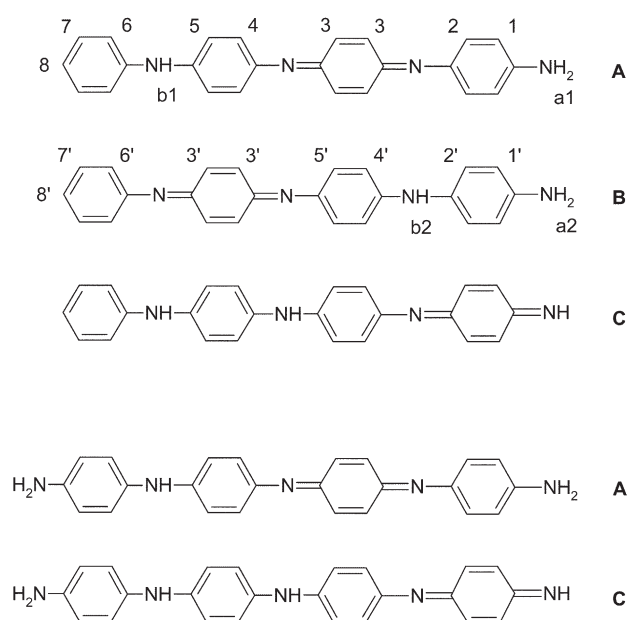
The oxidation of both tetramers can be confirmed by the IR spectra. The main difference between the spectra of tetramers in the leucoemeraldine state and that in the emeraldine state is the appearance of a peak at  $1596\text{ cm}^{-1}$  due to CC stretching

in the quinoid ring and a peak at  $1167\text{ cm}^{-1}$  ascribed to C–H bending deformations in the quinoid ring.<sup>14</sup> The mode related to C–H out-of-plane deformation is also displaced to  $832\text{ cm}^{-1}$  in the spectrum of oxidized  $\text{Ph}/\text{NH}_2$  tetramer **9** and to  $842\text{ cm}^{-1}$  in the spectrum of the oxidized  $\text{NH}_2/\text{NH}_2$  molecule **4** as compared to the case of the reduced tetramers.

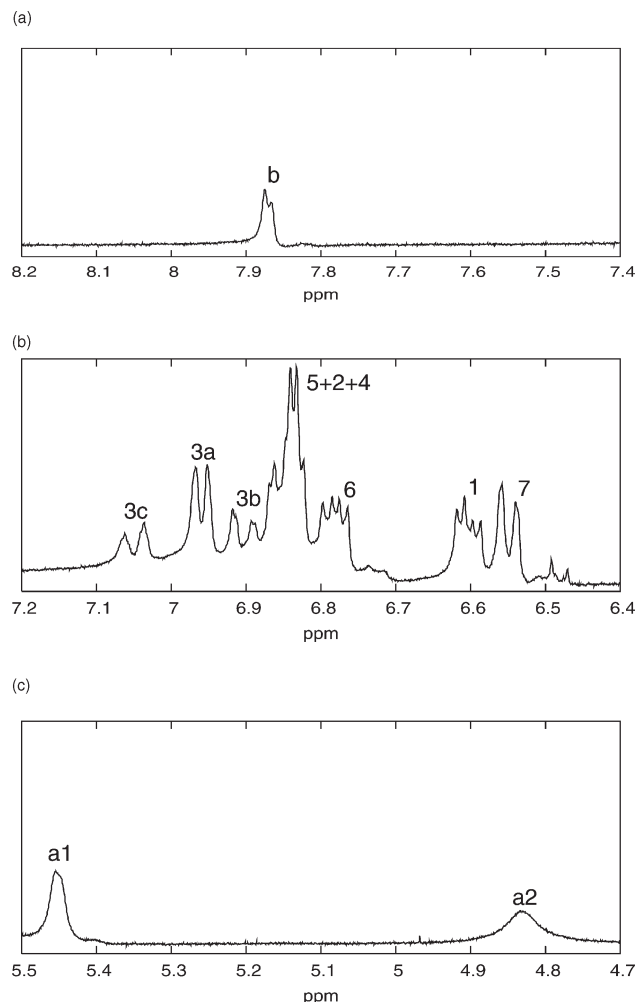
However, oxidation of tetramers can lead to the formation of different positional isomers, shown in Scheme 3, as was postulated by MacDiarmid *et al.*<sup>13</sup>. Tetramer  $\text{Ph}/\text{NH}_2$  can form three positional isomers. Tetramer  $\text{NH}_2/\text{NH}_2$  **4** is symmetric and can form only two isomers. The  $^1\text{H}$  NMR spectrum of oxidized  $\text{NH}_2/\text{NH}_2\text{-EB}$  tetramer **4** is shown in Fig. 4. The oxidation of this tetraamine to the emeraldine state causes the loss of symmetry. In the spectrum three signals at 7.86, 5.44 and 4.83 ppm can be attributed to amine protons. This suggests that after oxidation the molecule exists in the form of isomer A. The formation of isomer C can be excluded since its formation would lead to four signals. The appearance of quinoid ring and imine nitrogens in the structure of the molecule causes a displacement of the amine proton signals in comparison to the signals observed in the spectrum of the reduced tetraamine. The signals of terminal amine group protons are shifted from 4.60 ppm in the spectrum of reduced  $\text{NH}_2/\text{NH}_2$  tetraamine **3** to 4.83 and 5.44 ppm and can be assigned to  $\text{NH}_2$  protons of the groups located further and closer to the quinoid ring, respectively. The quinoid ring influences also the position of the signal of  $\text{-NH-}$  proton, which shifts from 7.08 ppm to 7.86 ppm upon the oxidation [compare Fig. 1(a) and Fig. 4]. Moreover, one can observe that except for the signal at 4.83 ppm all other signals are split. The simplest interpretation of these spectral features involves the presence of syn and anti isomers (see Scheme 4). We tried to interpret the spectrum according to this hypothesis and estimate the relative amounts of both isomers. We assumed that the signals, for example at 7.86 (7.85), 6.56 (6.54), 6.79 (6.76) are related to the same type of protons but in the anti and syn isomers. The ratio of the areas of the mentioned peaks is estimated as 1:0.75, thus the ratio of the amount of both isomers should be the same. Additionally, we assumed that the anti isomer, which has the lower steric hindrance, would be present in higher concentration. According to these assumptions the multiplets located at 6.56–6.54 ppm can be attributed to  $\text{H}_7$ , at 6.61–6.58 ppm to  $\text{H}_1$  and at 6.79–6.77 ppm to  $\text{H}_6$  protons. The intense and broad



**Fig. 3** The UV-Vis-NIR spectra in DMSO of (a)  $\text{NH}_2/\text{NH}_2$  tetramer **3**, (b)  $\text{Ph}/\text{NH}_2$  tetramer **8** oxidized with ammonium persulfate in 0.1 M HCl solution.

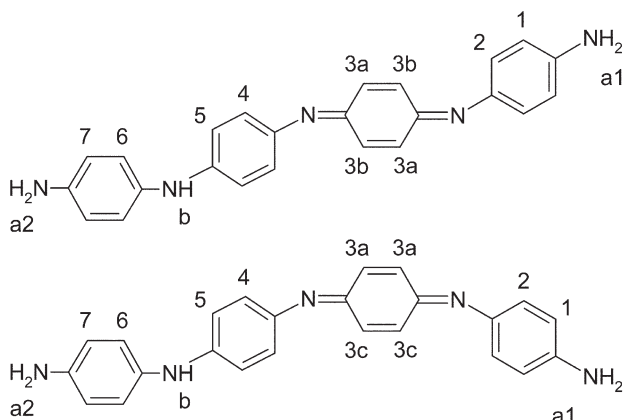


**Scheme 3** Positional isomers of oxidized  $\text{Ph}/\text{NH}_2$  and  $\text{NH}_2/\text{NH}_2$  tetramers.



**Fig. 4** The  $^1\text{H}$  NMR spectrum in  $\text{DMSO-d}_6$  of the  $\text{NH}_2/\text{NH}_2\text{-EB}$  tetramer **4**.

multiplet at 6.89–6.83 can be assigned to other protons of the phenylene rings. However, the assignment of the quinoid protons is not so clear. The peaks at 6.96 and 6.95 ppm can be ascribed to this type of proton but the integration of these peaks gave a too low value to correspond to four protons. Nevertheless, the quinoid protons are influenced by  $\text{H}_2$  and  $\text{H}_4$  protons and are not equivalent, as it is shown in Scheme 4. Thus, we can distinguish three types of protons marked as  $\text{H}_{3a}$ ,  $\text{H}_{3b}$  and  $\text{H}_{3c}$ . If the signals at 7.06–7.04 ppm and at 6.94–6.91 ppm are also due to the quinoid protons the area ratios of the signals 7.06–7.04 ( $\text{H}_{3c}$ ): 6.96–6.95 ( $\text{H}_{3a}$ ): 6.94–6.91 ( $\text{H}_{3b}$ ) ppm should correspond to 1.5:3.5:2, taking into

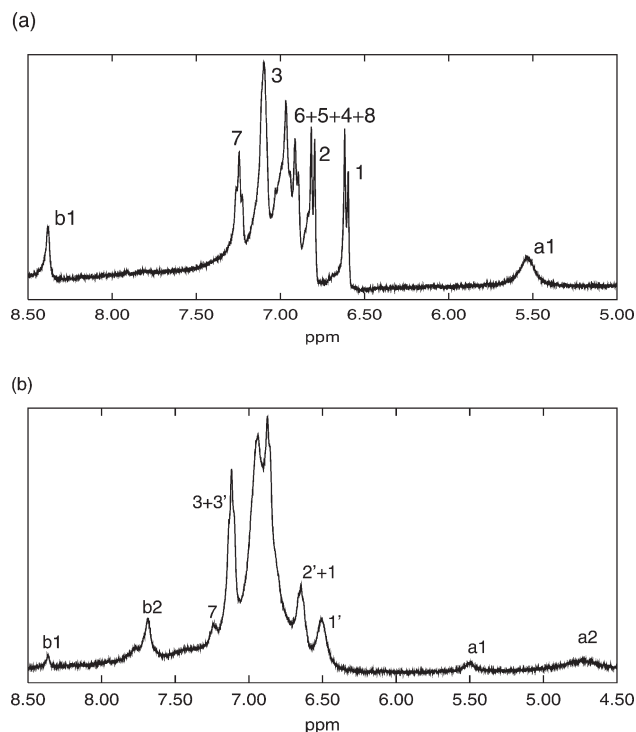


**Scheme 4** Anti and syn isomers of the oxidized  $\text{NH}_2/\text{NH}_2$  tetramer **4**.

consideration our earlier assumptions (anti-to-syn ratio of 1:0.75). The area ratios of the corresponding peaks measured from the spectrum is 1.6:3.4:2, which is in an agreement with our predictions.

We have also studied two  $\text{Ph}/\text{NH}_2$  tetramers in the emeraldine oxidation state, the  $\text{Ph}/\text{NH}_2\text{-EB(MD)}$  tetramer **10** obtained by oxidative coupling and the  $\text{Ph}/\text{NH}_2\text{-EB}$  tetramer **9** prepared by the  $\text{S}_{\text{N}}\text{Ar}$  coupling/reduction sequence and then oxidized. The  $^1\text{H}$  NMR spectra of both tetramers are shown in Fig. 5. It has been reported by MacDiarmid *et al.*<sup>13</sup> that in  $\text{DMSO-d}_6$  solution only isomer B was detected (see Scheme 3). Cao *et al.*<sup>15</sup> stated that in  $\text{DMF-d}_6$  solution the isomeric forms B and C co-exist. However, comparison of our spectrum of the  $\text{Ph}/\text{NH}_2\text{-EB(MD)}$  tetramer **10** with the spectrum of the  $\text{NH}_2/\text{NH}_2\text{-EB}$  tetramer **4** shows that only isomer A is formed. The signal of the terminal amino group protons are located at 5.53 ppm, similar to the case of the signal of  $\text{NH}_{2(a1)}$  in the spectrum of  $\text{NH}_2/\text{NH}_2\text{-EB}$  **4**, indicating a rather close vicinity of the quinoid ring. Additionally, the signal of the  $-\text{NH}-$  proton is placed at 8.38 ppm and is shifted *ca.* 0.68 ppm in comparison to the  $-\text{NH}_4^+$  signal observed at 7.70 ppm in the  $\text{Ph}/\text{NH}_2$  tetraamine **11** spectrum [see Fig. 1(b)]. A similar  $-\text{NH}-$  signal displacement is detected in the spectrum of the  $\text{NH}_2/\text{NH}_2\text{-EB}$  tetramer **4**. The signal at 7.09 ppm can be assigned to quinoid protons. The triplet at 7.24 ppm is ascribed to  $\text{H}_7$  protons. However, the second triplet of  $\text{H}_8$  was not clearly visible and we suppose that it could be located at *ca.* 6.83 ppm, overlapping with the signals of other aromatic protons. The assignment of other signals is marked in Fig. 5(a).

The spectrum [Fig. 5(b)] of the oxidized  $\text{Ph}/\text{NH}_2$  tetraamine in the EB state **9** is richer compared to that of  $\text{Ph}/\text{NH}_2\text{-EB(MD)}$  **10**. This spectrum can correspond to a mixture of the positional isomers A and B because two signals appear at 4.73 and 5.49 ppm, which can be related to the  $\text{NH}_{2(a2)}$  and  $\text{NH}_{2(a1)}$  protons. Moreover, two signals that can be attributed to  $-\text{NH}-$  protons are located at 7.68 and 8.36 ppm. The integration of the signals at 4.73/5.49 ppm gives the ratio 3.3:1 and the integration of the signals at



**Fig. 5** The  $^1\text{H}$  NMR spectra in  $\text{DMSO-d}_6$  of (a)  $\text{Ph}/\text{NH}_2\text{-EB(MD)}$  tetramer **10** and (b)  $\text{Ph}/\text{NH}_2\text{-EB}$  tetramer **9**.

7.68/8.36 ppm results in a 3.8:1 ratio. Thus, the isomer B is formed in preference to isomer A in this case. The signal at 7.12 ppm can be assigned to quinoid protons. The peak at 7.24 ppm can correspond to H<sub>7</sub> protons whereas the triplet of H<sub>7'</sub> should be more shifted and can overlap with the signal at 7.68 ppm (–NH<sub>b2</sub>).

It should be stressed that in the spectra of **9** and **10** presented in Fig. 5 the signals are not split as it is observed in the spectrum of **4** in Fig. 4. The question why we do not detect the syn and anti isomers in these cases remains open. The most trivial explanation is that only one type of isomer (syn or anti) is formed, however, other hypotheses cannot be excluded.

## Conclusions

Two types of aniline tetramers, namely NH<sub>2</sub>/NH<sub>2</sub> and Ph/NH<sub>2</sub> end-capped oligomers, were synthesized by an S<sub>N</sub>Ar coupling/reduction sequence. Additionally, the Ph/NH<sub>2</sub>-EB(MD) tetramer was obtained by oxidative coupling. The spectroscopic properties of these tetramers in the leucoemeraldine and emeraldine oxidation states were compared. In the reduced form both types of Ph/NH<sub>2</sub> tetraamines are spectroscopically indistinguishable. They differ, however, in the oxidized state. The oxidative coupling led to the formation of positional isomer A whereas the oxidation of the Ph/NH<sub>2</sub> tetraamine gave a mixture of isomers A and B. In the case of NH<sub>2</sub>/NH<sub>2</sub>-EB tetramer two geometrical isomers, syn and anti, were present.

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