Ladder Oligophenothiazines by Direct
Thionation of *N*-Arylanilino Derivatives

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Ladder oligophenothiazines were synthesized by direct catalyzed insertion of elemental sulfur in anilino-substituted phenothiazines and *para*-oligoanilines. The starting 3- and 3,7-anilino derivatives of phenothiazine were prepared with improved selectivities and yields by new syntheses. The oxidability of the oligomers is discussed.

Heteroaromatic ladder compounds of the phenothiazine-type have attracted much attention in the last few years because of their interesting electrical properties as well as non-linear optical activity [2-4]. For example, un-usually high conductivities were reported both for an un-doped polymer, 10^{-5}-10^{-6} Ω^{-1} cm^{-1} [2b], and oligomers, 10^{-7} Ω^{-1} cm^{-1} by us in a previous communication [5]. A condensation route is generally used to synthesize pheno-

Scheme 1
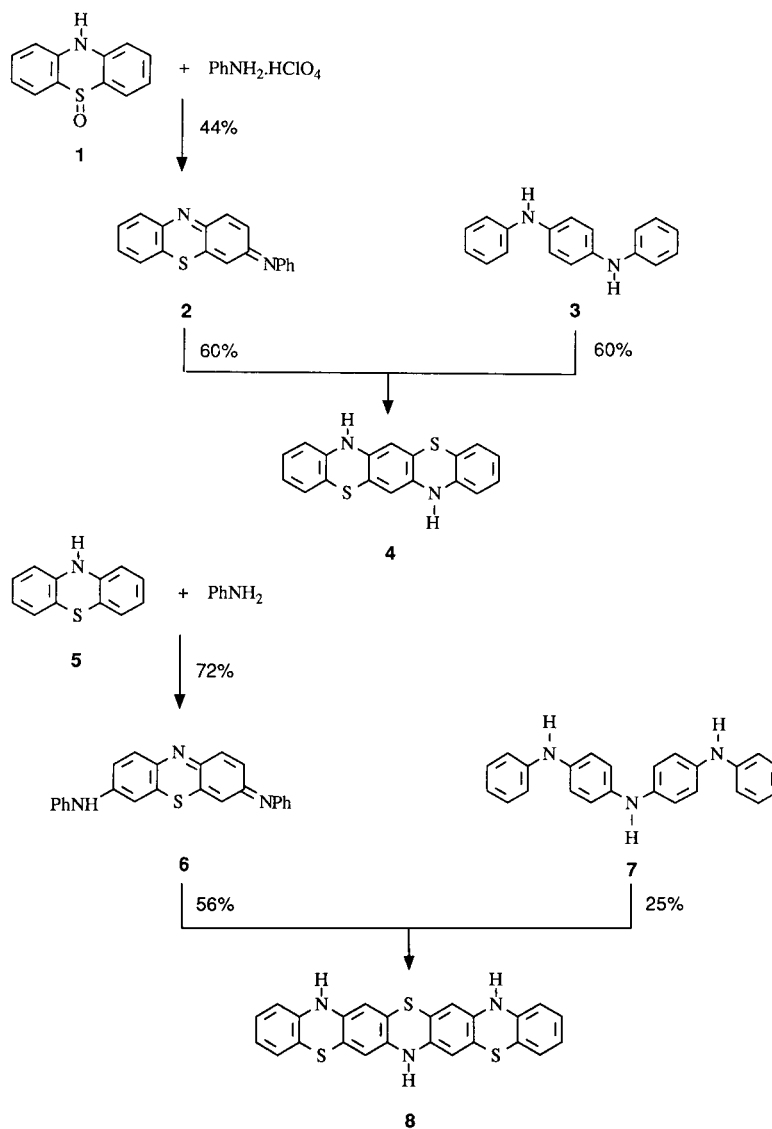
thiazine ladder structures starting from benzoquinones and arylamines, both of which require polyfunctionality [2b,4,6,7]. Recently, we reported an easy method for the preparation of a ladder phenothiazine oligomer, 4, by direct thionation with elemental sulfur of N,N'-diphenyl-p-phenylendiamine (3) [8]. In the present work we investigated the versatility of this simple synthesis, suitably improved, starting from other aniline compounds such as anilino-substituted phenothiazines 2 and 6, and para-oligoaniline 7 (Scheme 1). Another hitherto unknown ladder oligophenothiazine, 8, was easily prepared.

Results and Discussion.

For the preparation of the imino precursors 2 and 6, Kehrmann's method [9], based on oxidation of phenothiazine (5) with iron trichloride to phenazathionium cation (9) in the presence of aniline, was not used owing to the poor selectivity and yield. For example, 2 could be synthesized with only a 19% yield in spite of a modified separation and purification procedure. We obtained better results with the generation of the intermediate cation 9 by conversion of phenothiazine 5-oxide (1) with perchloric acid [10,11a] or by the oxidation of 5 with iodine via a charge-transfer complex [11b] (Scheme 2). The first method was found suitable for the synthesis of imine 2. The yield increases with increasing 5-oxide 1 to aniline ratios up to 1:2 (44% yield). With greater amounts of aniline, 6 begins to form and the reaction becomes specific neither for 2 or 6 preparation. The recovery of phenothiazine from the by-

products is an indication that a disproportionation reaction also takes place, limiting the concentration of 9. To synthesize imine 6 with a high yield (72%) it was necessary to react the cation in a basic medium instead of an acidic one. This was achieved by oxidizing 5 with iodine in the presence of a considerable excess of aniline. Not less than 6 moles of iodine per mole of 5 are required in the reaction; a probable reason may reside in the charge transfer complexation not only of phenothiazine but also of the product 6 with the oxidizing agent [12]. Further characterizations for 2 and 6, not adequately characterized by Kehrmann [9], are reported in the experimental part.

The thionation reaction of imines 2 and 6 was carried out in o-dichlorobenzene at boiling temperature with 5 moles of elemental sulfur for each ring closure, in the presence of iodine as the catalyst. Since the reaction was found to proceed on the leuco compounds and not on the quinone-imines, a flow of hydrogen sulfide was used, just before the reaction started, to reduce in situ 2 and 6 to the corresponding 3-anilinophenothiazine (10a) and 3,7-dianilinophenothiazine (10b). These latter compounds also were isolated and found to be easily oxidizable in air. The initial hydrogen sulfide was replaced by that evolved during the reaction. The same method also was employed for the thionation of oligoanilines 3 and 7 to maintain a reducing atmosphere. Excess sulfur, used to improve the yields, leads to adducts between oligophenothiazines and sulfur, very stable to continuous and prolonged extraction with hot carbon disulfide. Thus, in order to remove the remaining sulfur completely, its reduction to hydrogen sulfide with hot phenylhydrazine was necessary. At present the adduct structures are not yet understood; however, a defined stoichiometry could be deduced from the microanalysis, for example 3:4 for oligomer 8 and sulfur, and the ir spectra are identical to those of the heterocyclic component [8,13].

Scheme 2

1

↓ +H⊕, -H₂O

9

↑ -2e, -H⊕

5

10a   R= H

b   R= PhNH
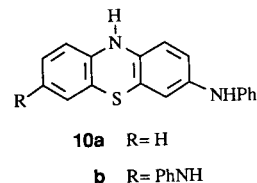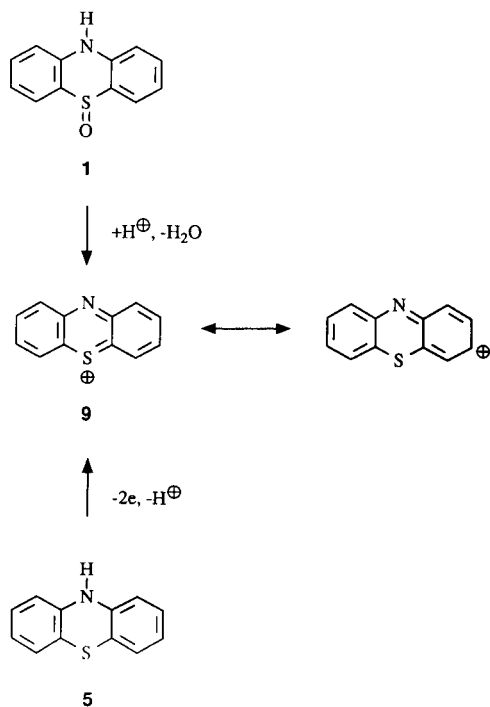
As shown in Scheme 1, independently of the starting anilino derivatives 2 and 3 or 6 and 7, the thionation route leads to the identical oligomer 4 or 8, respectively. As expected, the infrared spectra of both oligophenothiazines show similar patterns of characteristic bands. The linear structure of 8 is supported by the presence of the strong absorption at 854 cm⁻¹, that can be assigned to the out-of-plane bending vibration of isolated hydrogens of benzene rings, and by the lack of a band relating to the out-of-plane bending of two hydrogens, that allows angular structures to be excluded. The strong band at 737 cm⁻¹, due to the

out-of-plane bending of the four adjacent hydrogens of the terminal rings, and the coincidence of the spectral profiles of the two oligomers in the 2000-1650 cm^{-1} overtone region confirm the type of benzene ring substitutions. A very strong characteristic peak due to N-H stretching vibration is also observed at 3332 cm^{-1}.

Powders of the products **4** and **8** were filtered and stored under nitrogen to avoid darkening, because they are very sensitive to oxygen, and probably to light. Upon exposure to oxygen, their color changes from yellow to black violet or greenish blue, respectively, in a short time, but without changes in the ir spectra. On the contrary, brilliant yellow thin flakes of **4**, obtained by sublimation in nitrogen (350° and 10^{-2} torr), maintain their initial color in air. The formation of traces of the corresponding quinone-imine **11** (Scheme 3) seems to be responsible for the color change for **4** [5]. On the other hand, this last compound is very easily oxidized to **11** by a number of oxidants and in different conditions, for example by silver(I) oxide, chromium(VI) oxide, a hot solution of iodine, sublimation in air and 96% sulfuric acid. In particular, solubilization of **4** in the acid, followed by water dilution and neutralization with an aqueous base, provides a quinone-imine and not a sulfoxide derivative as phenothiazine does [14]. Previously, a sulfoxide structure was tentatively indicated by us [8] instead of compound **11** now clearly recognized. It should be emphasized that the product investigated corresponds fully to that obtained by Garbarczyk [15] but not equally well to the quinone-imine claimed by Okada and Marvel [6]. The electronic spectra of **4** and **11** in the concentrated acid are identical and can be referred to the protonated quinone-imine. Oxidation of **4** is also favored by the presence of a strong base as shown by formation of **11**, almost in quantitative yields, in aerated methanolic solutions of potassium hydroxide (see Experimental part). This may suggest that the anionic forms originated by deprotonation are more oxidizable than the starting product. A sample of **11** can again be transformed quantitatively in the leuco form **4** by stirring a suspension in phenylhydrazine at room temperature.

Scheme 3

4   **11**
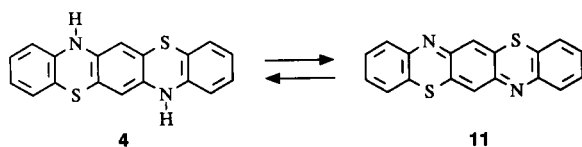
Comparing the electronic spectrum of the oligomer **8** in 96% sulfuric acid with that of **4** (Figure 1), a bathochromic shift, particularly evident for the peak in the visible region, is observed. This effect seems to suggest enhanced

delocalization as a result of the increased number of condensed rings. For both oligomers the conversion between leuco and oxidized forms was indicated by preliminary cyclic-voltammetric data [16] with reversible redox processes below 1 V. The oxidation peaks at 0.25 V and 0.08 V *versus* the Standard Calomelan Electrode for **4** and **8**, respectively, show that the latter oligomer is the most oxidizable. However, as yet, we have not been able to isolate a defined oxidized form for this compound.
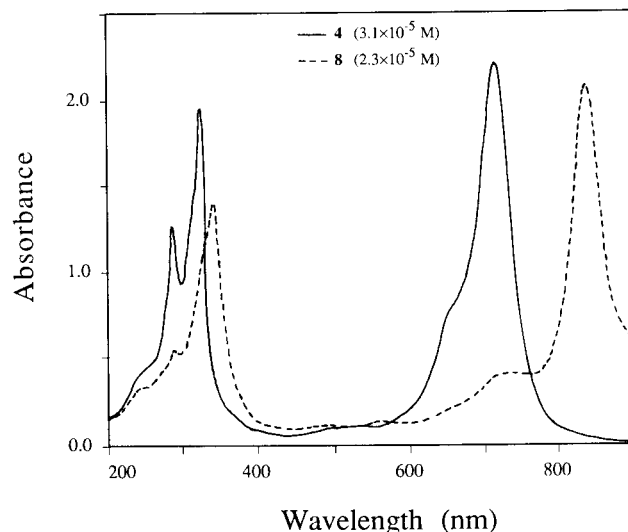

Figure 1. UV-visible spectra of oligophenothiazines in 96% sulfuric acid.

EXPERIMENTAL

Commercial phenothiazine (**5**) (99%, Merck) was used as received. Phenothiazine 5-oxide (**1**) was prepared by oxidation of **5** with hydrogen peroxide in dioxane [17]. Commercial aniline was distilled before use. Aniline perchlorate was precipitated from a mixture of 70% perchloric acid and aniline in tetrahydrofuran and recrystallized from 1-propanol. Commercial *N,N'*-diphenyl-*p*-phenylenediamine (**3**) (Aldrich) was recrystallized from ligroin and 95% ethanol. Trianilinobenzene (**7**) was synthesized by deamination of the leuco base of Willstätter's imine [18] according to the method given in the literature [19]. Anhydrous magnesium sulphate was used as desiccant.

The melting points were determined on a Büchi apparatus and are uncorrected; for the compounds **4**, **8** and **11** the determinations were carried out using a DSC-2C Perkin-Elmer differential scanning calorimeter under nitrogen with a heating rate of 20°/minute. The ir spectra (potassium bromide pellets) were recorded on a Perkin-Elmer 1750 FTIR spectrometer. The uv-visible spectra were measured with a Kontron UVIKOM 860 spectrophotometer. The molecular weights were determined by a VG 7070 E mass spectrometer. The elemental microanalyses were done in our laboratory with a Carlo Erba 1106 elemental analyzer and REDOX Laboratories, Cologno Monzese, Milano. Characterizations by nmr could not be made owing to insufficient solubility of the compounds.

3-Phenylimino-3H-phenothiazine (2).

A solution of perchloric acid (65% aqueous, 8.9 ml, 92.1 mmoles) in tetrahydrofuran (25 ml), cooled below 5°, was poured into a suspension of 1 (3.24 g, 15 mmoles) and aniline perchlorate (5.80 g, 30 mmoles) in tetrahydrofuran (20 ml). The reaction mixture was stirred for 6 hours at room temperature, then 9% hydrochloric acid (500 ml) was added and the final mixture extracted with chloroform (1 l). The separation of the two phases, very dark in color, was made easier by the addition of a saturated sodium chloride solution (maximum 200 ml). The chloroform layer was filtered to remove any suspended solids present, washed with 9% hydrochloric acid (250 ml x 2) and water, neutralized with 15% ammonium hydroxide and dried. After removal of the solvent at reduced pressure, the residue was purified by column chromatography over silica gel using chloroform as eluent to give 2 (1.9 g, 44%) as dark red powder, mp 150-151° (lit [9] mp 150°); ir: 1609, 1590, 1563, 1528, 1494, 1308, 1238, 1113, 1028, 856, 821, 769, 697 cm^{-1}; uv-vis (95% ethanol): 244 (log ϵ 4.14), 280 (4.27), 356 (4.04), 508 nm (4.08); ms: m/z 288 (M$^+$).

Anal. Calcd. for $C_{18}H_{12}N_2S$: C, 74.97; H, 4.19; N, 9.72; S, 11.12. Found: C, 74.67; H, 4.17; N, 9.68; S, 11.08.

7-Anilino-3-phenylimino-3H-phenothiazine (6).

A solution of aniline (18.6 g, 200 mmoles) in tetrahydrofuran (20 ml) was poured into a solution of 5 (4.0 g, 20 mmoles) and iodine (15.2 g, 120 mmoles) in tetrahydrofuran (50 ml) [20]. The reaction mixture was stirred for 6 hours at room temperature, then benzene (400 ml) was added and stirring maintained for an additional 18 hours. At the end, the mixture was let to stand in a refrigerator for a day and the precipitated dark brown product was filtered, washed with benzene and dried *in vacuo* to give 26.7 g of a crude likely mixed complex formed with 6, iodine and aniline [21]. This solid was divided into 5 g portions. Each portion was dissolved under vigorous stirring in a mixture of chloroform (500 ml), concentrated ammonium hydroxide (50 ml) and 5% sodium thiosulfate (20 ml). The organic layer was washed with water up to neutralization and dried. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel using first chloroform, followed by chloroform-diethyl ether (1:1, v:v) and then diethyl ether as eluents to give 6 (0.83 g, 72%) as black violet powder, mp 216-218°; ir: 3243, 1613, 1582, 1511, 1482, 1440, 1328, 1309, 1253, 1228, 1127, 875, 852, 805, 783, 750, 697 cm^{-1}; uv-vis (95% ethanol): 245 (log ϵ 4.20), 296 (4.58), 657 nm (4.65); ms: m/z 379 (M$^+$).

Anal. Calcd. for $C_{24}H_{17}N_3S$: C, 75.96; H, 4.52; N, 11.08; S, 8.45. Found: C, 75.66; H, 4.54; N, 11.04; S, 8.42.

Reactions of 2, 3, 6 and 7 with Elemental Sulfur.

The anilino derivatives 2, 3, 6 and 7 were reacted with the same procedure as described in the example below; powders of the products 4 and 8 were filtered and stored under nitrogen.

Bis[1,4]benzothiazino[2,3-b:3',2'-i]phenothiazine (8).

A suspension of 6 (1.0 g, 2.64 mmoles) in o-dichlorobenzene (10 ml) was heated at 150° under a flow of hydrogen sulfide until the color turned brown (ca. 2 hours). Then sulfur (0.85 g, 26.4 mmoles) and an o-dichlorobenzene solution of iodine (5 x 10^{-3} M, 0.3 ml) were added in that order. The mixture was refluxed under stirring and the flow of hydrogen sulfide was cut off. After 24 hours of reflux, the reaction mixture was cooled, diluted with car-

bon disulfide (30 ml) and the insoluble material removed by filtration and Soxhlet extracted with carbon disulfide for 24 hours. The residue was heated for several hours at 150° with phenylhydrazine (5 ml) until the evolution of hydrogen sulfide ceased. After cooling, the suspension was diluted with ethyl acetate, filtered and washed with the same solvent up to the elimination of phenylhydrazine, giving 8 (0.65 g, 56%) as dirty yellow powder. The same compound was obtained from 7 (0.89 mmoles in 10 ml of o-dichlorobenzene) in 25% yield after 65 hours of reflux; ir: 3332, 1588, 1576, 1492, 1474, 1431, 1302, 1284, 854, 737 cm^{-1}; uv-vis (96% sulfuric acid): 286 (log ϵ 4.39), 337 (4.79), 835 nm (4.96); ms: m/z 441 (M$^+$).

Anal. Calcd. for $C_{24}H_{15}N_3S_3$: C, 65.28; H, 3.42; N, 9.52; S, 21.78. Found: C, 65.02; H, 3.43; N, 9.48; S, 21.69.

[1,4]Benzothiazino[2,3-b]phenothiazine (4).

This compound was obtained from both 2 and 3 (3.47 mmoles and 3.84 mmoles in 10 ml of o-dichlorobenzene, respectively) in 60% yield as yellow powder, mp 411°; it can be recrystallized from phenylhydrazine after solubilization at 150°; uv-vis (N,N'-dimethylpropyleneurea-ethanol, 1:500, v:v): 229 (log ϵ 4.27), 270 (4.77), 336 nm (3.90); (96% sulfuric acid): 284 (log ϵ 4.61), 320 (4.80), 713 nm (4.85); ms: m/z 320 (M$^+$). The ir spectrum and the elemental analysis are in agreement with the previous data [8].

3H,10aH-[1,4]Benzothiazino[2,3-b]phenothiazine (11).

A suspension of 4 (1.0 g, 3.12 mmoles) in a solution of potassium hydroxide (0.438 g, 7.81 mmoles) in methanol (500 ml) was refluxed for 6-7 days up to the complete disappearance of the N-H stretching band at 3332 cm^{-1}. The residue was filtered, washed with water up to neutralization and then with very little methanol to give 11 (0.94 g, 95%), as violet thin plates with a golden luster, which was sublimed at 165° and 0.3 torr, mp 317° (lit [15] mp 321°); ir: 1497, 1437, 1055, 760, 754, 719, 535 cm^{-1}; uv-vis (96% sulfuric acid): 283 (log ϵ 4.52), 320 (4.74), 715 nm (4.85); ms: m/z 318 (M$^+$).

Anal. Calcd. for $C_{18}H_{10}N_2S_2$: C, 67.89; H, 3.17; N, 8.80; S, 20.14. Found: C, 67.87; H, 3.16; N, 8.76; S, 20.06.

REFERENCES AND NOTES

[1] Current address: Istituto di Merceologia, Università di Bologna, 40126 Bologna, Italy.

[2a] O.-K. Kim, *Mol. Cryst. Liq. Cryst.*, **105**, 161 (1984); [b] O.-K. Kim, *J. Polym. Sci., Polym. Letter Ed.*, **23**, 137 (1985); [c] M. D. Pace and O.-K. Kim, *Synth. Metals*, **25**, 333 (1988).

[3] D. R. Ulrich, *Polymer*, **28**, 533 (1987).

[4a] L. R. Dalton, J. Thomson and H. S. Nalwa, *Polymer*, **28**, 543 (1987); [b] L. R. Dalton, R. Montgomery, C. L. Young, P. H. Bryson and Y. P. Yu, Preprints of the Europian Symposium on Polymeric Materials (Polymers for Electronics), Lyon, France, 1987.

[5] C. Della Casa, F. Andreani, P. Costa Bizzarri, M. Fiorini, E. Salatelli, L. Grossi and W. Porzio, *Synth. Metals*, **29**, E477 (1989).

[6] M. Okada and C. S. Marvel, *J. Polym. Sci. A-1*, **6**, 1774 (1968).

[7] R. L. Mital and S. K. Jain, *J. Chem. Soc. (C)*, 1875 (1971). 1875.

[8] C. Della Casa, P. Costa Bizzarri and F. Andreani, *Synth. Metals*, **18**, 381 (1987).

[9] F. Kehrmann and O. Vesely, *Liebigs Ann. Chem.*, **322**, 39 (1902).

[10] J.-P. Billon, *Ann. Chim.* (Paris), **7**, 183 (1962).

[11a] C. Bodea and I. Silberg, in Advances in Heterocyclic Chemistry,

Vol **9**, A. R. Katritzky and A. J. Boulton, eds, Academic Press, New York, 1968, p 348; [b] idem, p 392.

[12] A complex with 1:4 stoichiometry between a pure sample of **6** and molecular iodine was obtained by precipitation in chloroform.

[13] E. A. Nodiff and P. N. Craig, *J. Org. Chem.*, **26**, 824 (1961).

[14] R. R. Gupta and Mahendra Kumar, in Phenothiazines and 1,4-Benzo-thiazines, R. R. Gupta, ed, Elsevier Science Publishers, Amsterdam, 1988, p 328.

[15] J. Garbarczyk, *Acta Cryst.*, **C41**, 1062 (1985).

[16] M. Leite de Almeida, private communication.

[17] C. Bodea and I. Silberg, *Studii Cercetari Chim* (Cluj), **14**, 317 (1963); *Chem. Abstr.*, **62**, 14664h (1965).

[18] R. Willstätter and C. W. Moore, *Ber.*, **40**, 2665 (1907).

[19] J. Honzl and M. Tlustakova, *J. Polym. Sci. C*, **22**. 451 (1968).

[20] The preformed solid complex between phenothiazine and iodine 2:3 was also used but gave lower yields.

[21] The presence of aniline in the mixed complex was checked by thin layer chromatography after the iodine separation.