FREE RADICALS OF PHENOTHIAZINE AND RELATED COMPOUNDS.VI-FREE RADICALS AND CHARGE TRANSFER COMPLEXES OF SOME OLIGOPHENOTHIAZINES.[1]

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ABSTRACT: The paper reports the synthesis of 1,4-benzothiazino[2,3-b]-phenothiazine 2 and its dibenzoanalogue: dibenzo[c,l]-16H,18H-triphenodithiazine 4 by the thionation of the N,N'-diphenyl-m-phenylene-diamine and N,N'-di(2-naphthyl)-m-phenylene-diamine respectively, with sulfur in the presence of iodine as catalyst.Chemical properties as N-acylation and CT complexes formation with various acceptors, are presented.The easy electrochemical oxidation at low potentials is shown by cyclic voltammetry. The free radicals formation is investigated by ESR spectroscopy.

INTRODUCTION

Continuing our investigations on the electrono-donor properties of the phenothiazine nucleus (1), we synthesised new heterocyclic compounds with repetitive phenothiazine nuclei, like 1,4-benzothiazino-[2,3-b]-phenothiazine 2 and its dibenzoanalogue 4,which could generate radicals and radical ion salts with an enhanced stability provided by the opportunities for electronic delocalisation, and which might generate CT complexes - organic electrono conducting materials, knowing the semiconductor properties already reported for the analogous ladder compounds (2),(3) with alternative disposition of the nitrogen and sulfur atoms.

RESULTS AND DISCUSSION

Synthesis.We obtained the N,N'-diphenyl-m-phenylene diamine 1 in moderate yield, by condensation of resorcinol with aniline in the presence of zinc chloride; the thionation of this compound with sulfur was carried out in xylene in the presence of iodine as catalyst (1%),scheme 1.
The 1,4-benzothiazino-[2,3-b]-phenothiazine 2 thus obtained is a brownish

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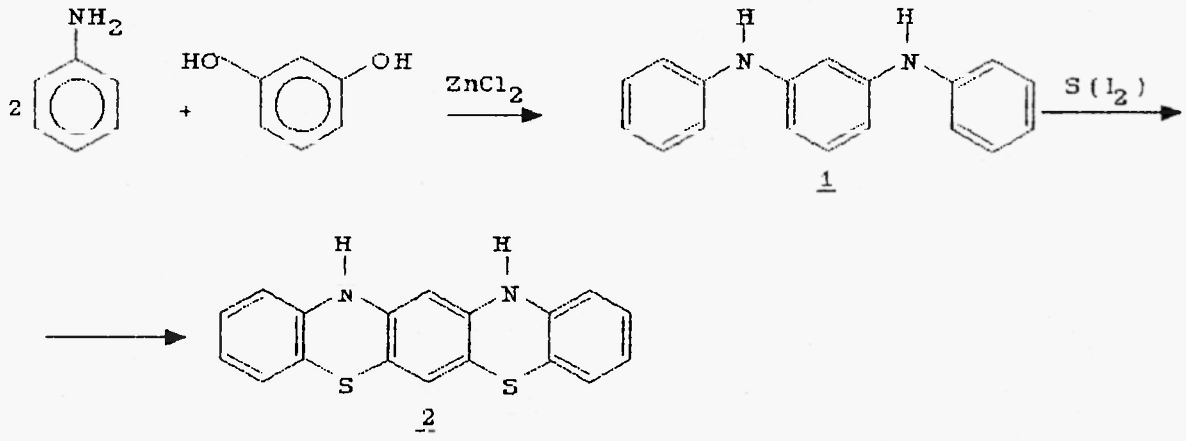
[1] The paper is dedicated to Prof. Dr. FRITZ SAUTER, Technical University Vienna, for his 65th anniversary.

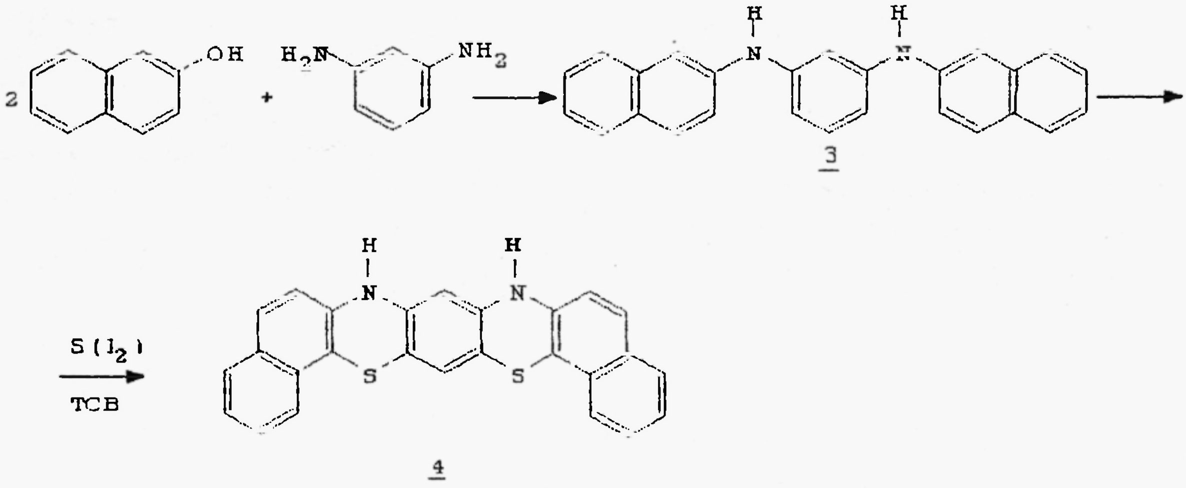
solid (m.p. 293°C).

The structure was elucidated by 300 MHz ^{1}H-NMR-spectroscopy. The protons bound to the nitrogens (δ= 8,85 ppm) are equivalent and the molecule displays a high symmetry.



Scheme 1

The analogous N,N'- di(2-naphthyl)-m-phenylene diamine 3 was obtained (4) by condensation of m-phenylene diamine with β-naphthol at 330°C, scheme 2, as white needles (m.p. 193°C).



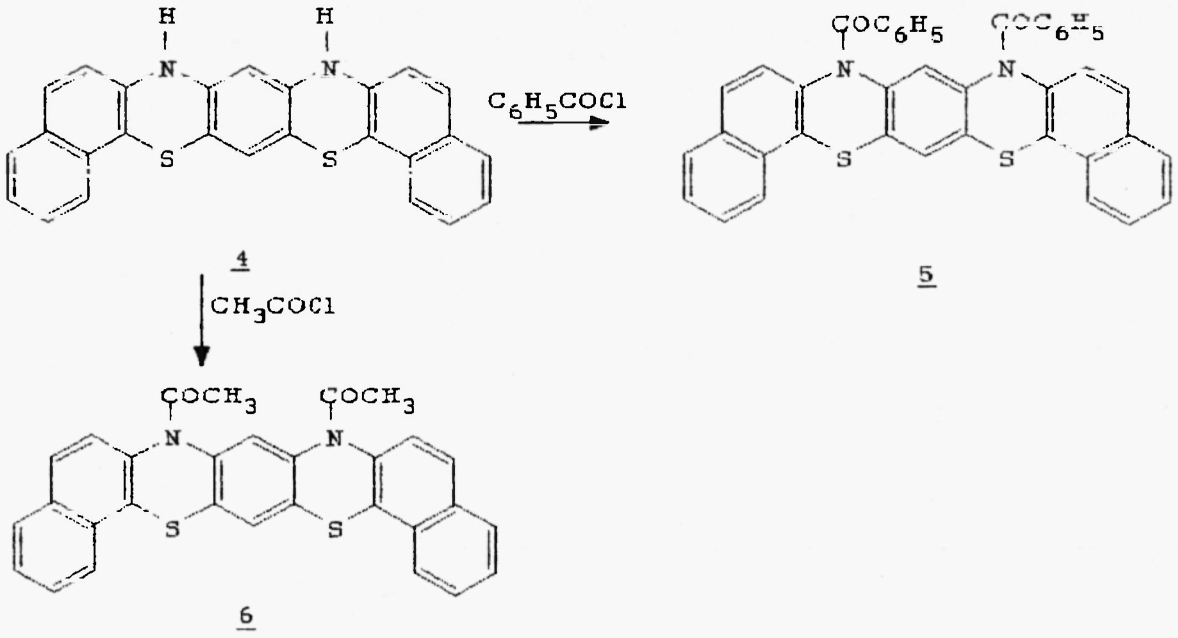
Scheme 2

The thionation of the N,N'-di(2-naphthyl)-m-phenylene diamine with sulfur in 1,2,4-trichlorobenzene as a solvent at 160°C, yielded 16H,18H-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene 4, which is a greenish crystaline product (m.p. 290°C with decomposition). It can be purified by recrystallisation from DMF.

The analysis of this reaction product was performed by: mass spectrometry - the molecular weight found was 420 - ^{13}C NMR spectroscopy, which showed 14 signals for the 26 carbon atoms in the molecule, due to the symmetry of the structure, and ^{1}H NMR-2D (COSY 45) at 300 MHz, which completely elucidated the structure.

The phenothiazine ring closure took place in the α positions of the naphthalenic nuclei, which generated the angular structure. The protons bound to the nitrogen atoms are also equivalent and they give sharp signals. 4 is a very stable compound. It is not soluble in benzene, acetone and chloroform, poorly soluble in DMSO and fairly soluble in DMF.

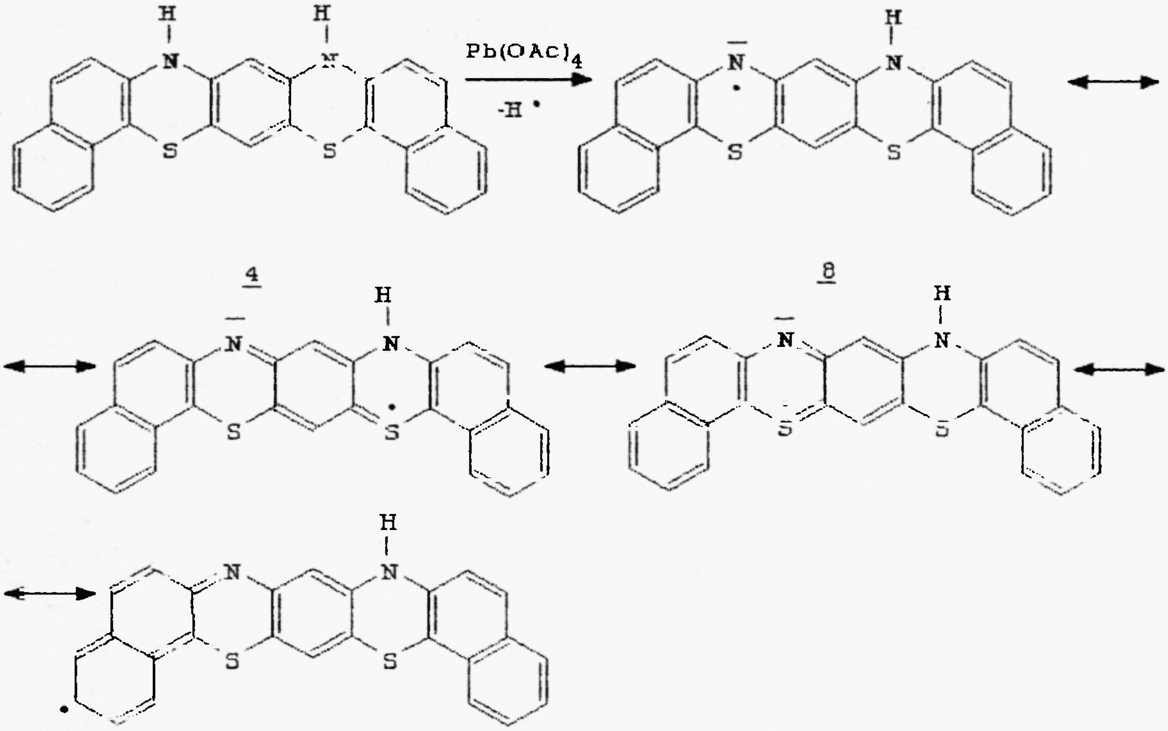
In order to further characterize the compound and to provide material for a stereochemical study we carried out the reaction of 4 with benzoyl chloride, scheme 3, which yielded the N,N'-dibenzoyl-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene 5, a white, well crystallised product (m.p. 301°C).



Scheme 3

Acetylation of the same heterocycle with acetyl chloride, scheme 3, yielded the N,N'-diacetyl-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene 6, which is also a white solid product (m.p. 294°C). We also tried acetylation with acetic anhydride, but it failed, a fact which points out the deep alteration of the secondary amine character owing to the inclusion in the heterocyclic system. Both products 5 and 6, were analysed by IR spectroscopy, which showed no absorption in the 3300 cm^{-1} region, where the heterocycle 4 had a medium absorption; we also found the characteristic wave number to the amidic carbonyl group absorption, 1650 cm^{-1}.

Chemical and electrochemical oxidation. The oxidation of 4, scheme 4, with lead tetraacetate, followed by the recording of ESR spectra of the generated radical, gave a triplet pattern, which can be explained by the formation of the neutral radical 8; assignement of hyperfine splittings to one nitrogen nucleus only, with no interference of the proton and of the other nitrogen atom is justified by the possible mesomeric structures listed in scheme 4.

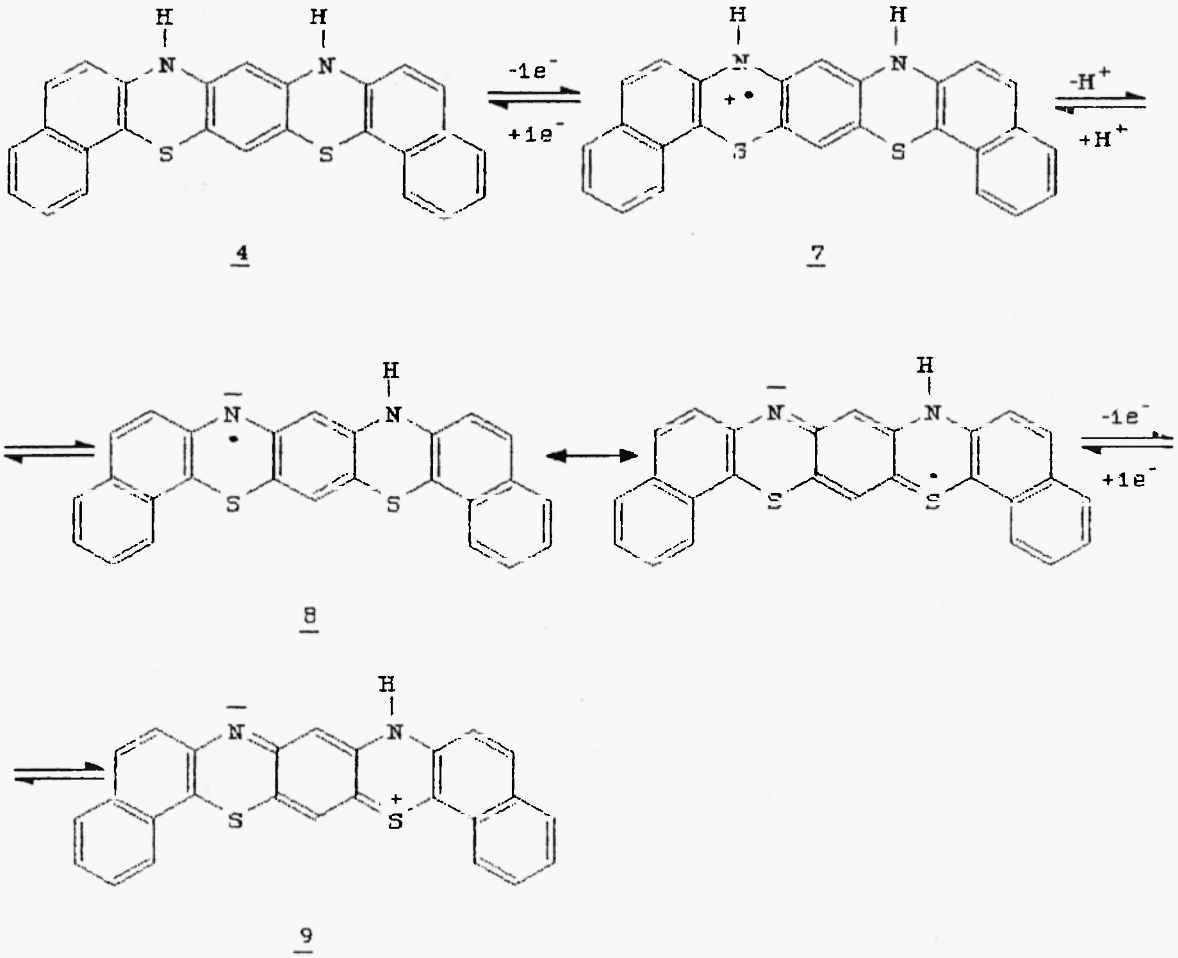


Scheme 4

Delocalisation of the electronic spin upon sulfur atoms cannot be seen in the sample with low natural abundance of ^{33}S nuclei.The hyperfine splittings due to the protons attached to the aromatic rings seem to be too small for the resolution of our instrument; the unfavourable energetics of mesomeric structures involving perturbation of aromaticity, accounts for this situation.

The same ESR spectral pattern was obtained when we analysed complexes of 4 with: tetracianoquinodimetane, TCNQ, (dark blue solid, m.p. 316-320°C), 3-nitro-phenothiazine-sulfoxide (black powder) and 1,3,7,9-tetranitro-phenothiazine-sulfoxide (black powder) in perchloric acid. All of the three complexes appear to contain the same neutral radical 8.

The processes of oxidation leading to the species 7-9, scheme 5, were independently investigated by cyclic voltammetry which demonstrated the reversibility of the redox phenomena. We propose for these facts an explanation based on scheme 5.



Scheme 5

The rapid two electrons release generates the stable cation 9 at a potential of 750 mV. The reversible reduction process shows two steps, the intermediates being the neutral radical 8 and the protonated cation radical 7 -fig.1a-

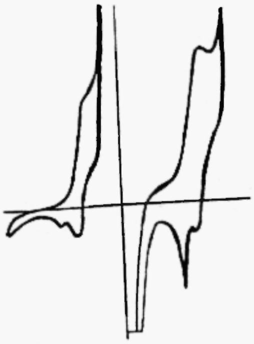


Fig.1 Cyclic voltammograms of 4 , electrolyte tetrapentylammonium bromide,electrode Pt., reference electrode Ag/Ag$^+$ a) in DMF, b) in DMF and acetic acid

In the presence of acetic acid, the peak attributed to the cation radical 7 is significantly more intense, so that we assume that its reduction occurs at a potential of 520 mV.

A comparison of species 7-9 with their counterparts in the chemistry of the phenothiazine ring clearly stresses the enhanced stability provided by the opportunities for electronic delocalisation made possible by the structures of the oligophenothiazine heterocyclic system.

Electronic spectra. Figure 2 shows the electronic spectra, which allows to distinguish the heterocycle 4 from its cation radical 7 and neutral radical 8. We attributed the absorption at λ_{max}= 500 nm (fig.2c) to the neutral radical 8, because it was obtained by recording the spectra of the complex of 4 with TCNQ dissolved in DMF. This is obviously different from the spectrum with a band at λ_{max}= 410 nm (fig.2b), showed by the solution of 4 in acetic acid after exposure to visible light for two days and attributed by us to the protonated cation radical 7; the same maxima were obtained in sulfuric acid solutions. The heterocycle 4, immediately after solving in DMF shows a λ_{max}= 350 nm (fig.2a). It can be noted that the exposure of this solution to the visible light for a few hours determines change in colour from yellow to red; the λ_{max} thus measured indicates the value 500 nm - the same as for the complex of 4 with TCNQ - assigned to the neutral radical 8. The sulfoxide of the heterocycle 4 upon reaction with perchloric acid, generates the cation 9 showing λ_{max}= 650 nm (a green solution in DMF),fig.2d. The analysis of these electronic spectra led us to the conclusion that the heterocycle 4 easily generates the neutral radical 8 even upon visible light absorption; in protic media, the radical exists mainly in the protonated form as a cation radical 7.

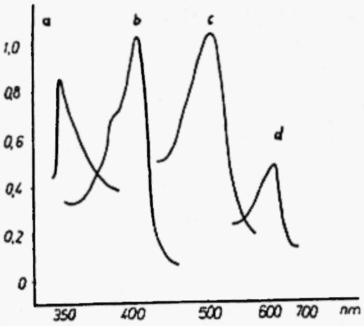


Fig.2 UV-VIS spectra for: a) heterocycle 4, b) cation radical 7, c) neutral radical 8, d) cation 9

EXPERIMENTAL

General: All commercial solvents were of p.a. grade quality. Melting points are given uncorrected. ^{1}H NMR spectrometer Brucker 300 MHz. EPR spectrometer IFA Bucharest. UV-VIS spectrometer Specord.

1,4-benzothiazino[2,3-b]-phenothiazine. 0,4 g N,N'-diphenyl-m-phenylene diamine, 0,2 g sulfur, one crystal iodine and 1 ml xylene were mixed and heated to reflux. A brownish precipitate starts accumulating as soon as the boiling begins. After refluxing for 30 min, the poorly soluble precipitate was extracted four times with hot o-dichlorobenzene (portions of 10 ml each) in the presence of a few drops of phenylhydrazine. The yellow grenish precipitate separates after cooling from the o-dichlorobenzene extracts was mixed and recrystallised from a small amount of nitrobenzene, washed with ethanol and dried to yield 0.25 g (50 %), m.p. 293^{0}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 6.18 (s, 1H), 6.51 (s, 1H), 6.64-6.82 (m, 4H), 6.7 (d, J=7.6 Hz, 2H),6.92-7.2 (m, 2H), 8.6 (s, 2H).

16H,18H- dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene (DDDP). 0.027 mol N,N'-di(2-naphthyl)-m-phenylene-diamine are heated together with 0.096 mol sulfur and 1% iodine in 100 ml 1,2,4-trichlorobenzene. At about 150^{0}C begins the H_2S evolving and a green precipitate separates from the solution. After the gas evolving ceased, the precipitate was filtered out, washed with chloroform and dried; yields 7.9 g (70%) DDDP insoluble in chloroform and benzene, soluble in DMF. After recrystallisation from DMF, m.p.290^{0}C with decomposition. IR: 3330 cm^{-1} ; ^{13}C NMR (300 MHz, DMSO-d_6) δ (ppm) = 101.1, 107.4, 108.1, 116.7, 121.4, 123.2, 123.8, 126.8, 127.1, 128.2, 129.4, 129.7, 139.2, 142.1; ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm) = 6.25 (s, 1H), 6.76 (s, 1H), 7.08 (d, J=8.7 Hz, 2H), 7.34 (m, 2H), 7.50 (m, 2H), 7.65 (m, 4H), 7.76 (d, J=8 Hz, 2H), 8.85 (s, 2H).

16,18-dibenzoyl-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene(benzoyl-DDDP). 0.035 mol DDDP are refluxed for 2 hours with an excess of benzoyl chloride (10 ml). The reaction mixture is then pourred into water and ice and the precipitate is filtered. The benzoic acid is removed by dissolving in hot water. The grey precipitate 1,6 g (71.4%) is purified by recrystallisation from acetic acid; the white precipitate thus obtained has m.p. 301^{0}C, IR: ν_{CO}= 1675 cm^{-1}, no absorption near 3300 cm^{-1}.

16,18-diacetyl-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene (acetyl DDDP). 0.0027 mol DDDP are refluxed for 2 hours with an excess of acetyl chloride. After pourring the reaction mixture into ice and water, the white precipitate is filtered and dried; yields 0,5 g (45%), m.p.299^{0}C, IR: ν_{CO}=1685 cm^{-1}, no absorption near 3300 cm^{-1}.

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Received June 12, 1995