MOLECULAR ORBITAL CALCULATIONS AND PHYSICAL PROPERTIES OF 1,4-BENZOTHIAZINO[2,3-*b*]PHENOTHIAZINE AND ITS SUBSTITUTED DERIVATIVES.

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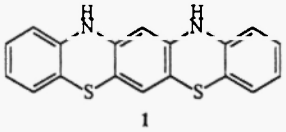
ABSTRACT: Synthesis of 12*H*,14*H*-3,9-dimethyl-5,7-dithia-12,14-diazapentacene **2** and molecular orbital calculations for 1,4-benzothiazino[2,3-*b*]phenothiazine **1** (parent heterocycle), its methylated derivative **2** and its dibenzoderivative 16*H*,18*H*-dibenzo[*c,l*]-7,9-dithia-16,18-diazapentacene **3**, are described. Spectral properties (UV-VIS, NMR and ESR spectra) showed good agreement with the theoretical calculations.

INTRODUCTION

In our previous work (1), we reported the synthesis of the new heterocycle 1,4-benzothiazino[2,3-*b*]-phenothiazine **1** and of its dibenzoderivative 16*H*,18*H*-dibenzo[*c,l*]-7,9-dithia-16,18-diazapentacene **3**, by the thiation with sulfur of the corresponding *N,N'*-diarylsubstituted-1,3-phenylenediamine, in the presence of iodine as catalyst. The chemical and electrochemical oxidation of **3**, (1-3), demonstrated the good electron donor properties of this compound. In this paper, the results of the theoretical calculations for the parent heterocycle **1** and for its dimethylated and dibenzoderivative **2** and **3** are presented. The correctness of these calculations is proved by the electronic and magnetic resonance spectra of the compounds under investigation.



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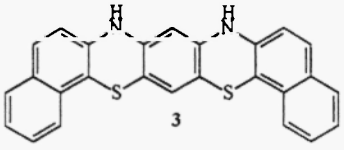

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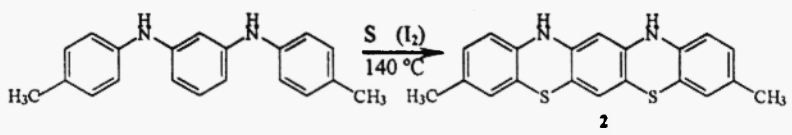
RESULTS AND DISCUSSION

12*H*,14*H*-3,9-Dimethyl-5,7-dithia-12,14-diazapentacene **2**, was synthesized by the thiation of *N,N'*-di(*p*-tolyl)-1,3-phenylenediamine with sulfur in the presence of iodine in catalytic amounts, using 1,2,4-trichlorobenzene as a solvent (scheme 1), the H_2S evolution appeared at aprox. 140 ^{0}C.



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Scheme 1.

The structure of **2** was assigned from mass spectrum (molecular peak at m/e = 348), and ^{1}H NMR spectrum recorded at 300 MHz. The protons at the central aromatic ring appear as two singlets at 6.12 ppm and 6.46 ppm, respectively. The protons in the two terminal benzene rings appear as a pair of doublets at 6.56, and 6.8 ppm. The *NH* group protons are also equivalent (like in structures **1** and **3**) and their signal appear at 8.6 ppm. The stretching vibrations of *NH* groups appear at 3460 and 3390 cm^{-1}.

The spatial structure of 1,4-benzothiazino[2,3-*b*]phenothiazine appears twice folded along the two parallel imaginary axes, each of them passing through the *N* and *S* atoms of the same thiazine ring, due to the bond angles of these heteroatoms. As a phenothiazine analogue, the 1,4-benzothiazino[2,3-*b*]phenothiazine has to prefer the *H intra* configuration (4) of the thiazine rings, because of the possible conjugation between nitrogen lone pair of electrons and the benzene π systems situated in its neighbourhood; from this point of view, the *H-extra* configuration (with sterical hindrance of this conjugation) seems less probable.

The evidence that the two *NH* groups from the structure **1**, **2** or **3** have the same spatial arrangement has been furnished by the ^{1}H NMR spectra, which show the magnetic equivalence of these protons (which appear at 8.9 ppm in **1**, 8.6 ppm in **2** and 8.86 ppm in **3**).

With the *H-intra* configuration for both *NH* groups in the 1,4-benzothiazino[2,3-*b*]phenothiazine nucleus, two diastereoisomers can appear (fig. 1), one of them having the reversed configurations of the two nitrogen atoms (the two lone pairs of electrons situated on the same part of the central planar benzene ring: "*cis* isomer") and the other one having the two nitrogen atoms with the same configuration (the two lone pairs of electrons situated on opposite parts of the central planar benzene ring: "*trans* isomer").

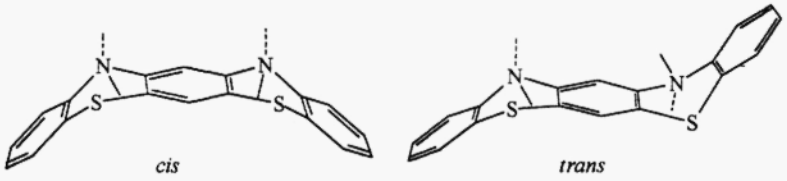

Figure 1

With HYPER CHEM program we calculated the heat of formation for both isomers of **1**, **2** and **3**; the obtained values are presented in Table 1; in all cases the "*cis* isomer" is slightly less stable than the "*trans* isomer". With the same program we calculated the molecular orbital energies (eV) for the 106 molecular orbitals of **1**, 118 molecular orbitals of **2** and 142 molecular orbitals of **3**. Table 2 shows the calculated energies

for the frontier orbitals of **1**, **2** and **3** and it can be seen that the smallest HOMO - LUMO energy difference appears for the dibenzoderivative **3** which seems to be the most reactive in the series.

Table 1. Calculated heats of formation for 1,4-benzothiazino[2,3-*b*]phenothiazine and its substituted derivatives

Compound	H_f [kcal/mol] "*cis* isomer "	H_f [kcal/mol] "*trans* isomer"	$\Delta H_{cis\text{-}trans}$ [kcal/mol]
1,4-benzothiazino[2,3-*b*]phenothiazine **1**	96.529	96.432	-0.097
12*H*,14*H*-3,9-dimethyl-5,7dithia-12,14-diazapentacene **2**	77.777	77.729	-0.048
16*H*,18*H*-dibenzo[*c,l*]-7,9-dithia-16,18-diazapentacene **3**	135.530	135.520	-0.010

The methylation of the parent heterocycle **1** does not modify this HOMO - LUMO energy difference.

Table 2. Calculated energies for the frontier orbitals of 1,4-benzothiazino[2,3-*b*]phenothiazine and its substituted derivatives

Compound		Energy [eV]		$\Delta E_{HOMO\text{-}LUMO}$
		HOMO	LUMO	
1,4-benzothiazino[2,3-*b*]-phenothiazine **1**	*cis*	-7.72	-0.60	7.12
	trans	-7.76	-0.60	7.16
12*H*,14*H*-3,9-dimethyl-5,7dithia-12,14-diazapentacene **2**	*cis*	-7.67	-0.57	7.10
	trans	-7.71	-0.57	7.14
16*H*,18*H*-dibenzo[*c,l*]-7,9-dithia-16,18-diazapentacene **3**	*cis*	-7.61	-0.86	6.75
	trans	-7.69	-0.87	6.82

The UV-VIS spectra of **1**, **2** and **3** are in good agreement with these theoretical values. Each of the three compounds presents only one absorption band situated in the UV range of the electromagnetic spectrum, with maxima at 290, 295 and 320 nm respectively. The methyl derivative **2** and the parent heterocycle **1** present almost the same position of the maxima of the absorption bands; the dibenzoderivative **3** presents an absorption band bathochromically shifted, as compared to the absorption maxima of **1**.

The bond lenghts in dibenzoderivative **3** and in its neutral radical have been calculated by using the PC SPARTAN program. Fig. 2 shows these calculated values, which are in good agreement with the information obtained from ESR spectrum.

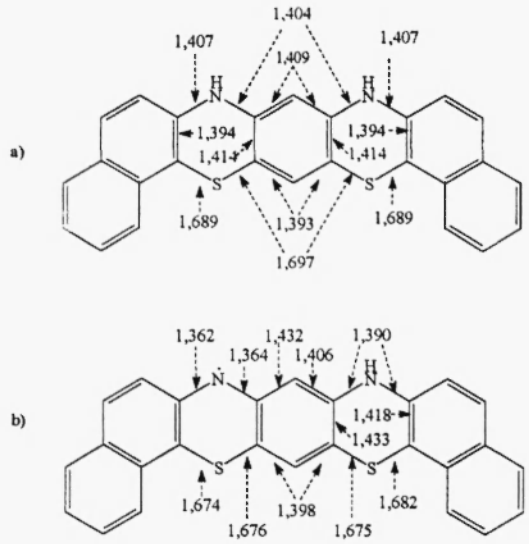

Fig. 2. Bond lenghths (Å) in: a) compound **3**, b) neutral radical of **3**

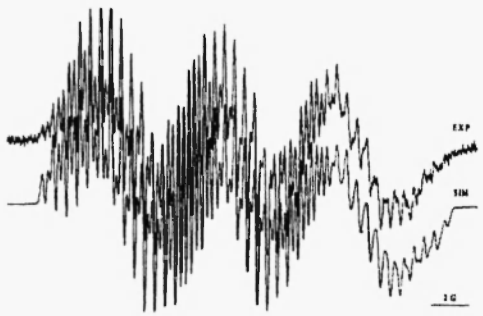

Fig. 3. Experimental and simulated ESR spectra of compound **3**

According to the hyperfine splytting observed in the ESR spectra of the neutral radical of **3**, there is a good agreement between *C-N*˙ bonds shortening (0,045 Å) and a smaller *C-NH* bond shortening (0,014 Å) in the neutral radical as compared to the parent heterocycle, representing the partial conjugation of the unpaired electron with the neighbouring naphthyl part of the molecule and the central benzene nucleus only. Figure 3 represents the ESR spectrum of the neutral radical of **3** and Table 3 presents the determined coupling constants.

Table 3 Coupling constants (in G) for the neutral radical of **3**

Coupling constants	a_N	a_N	a_H	a_H	a_H	a_H	a_H	a_H	a_H	a_H
(G)	5.82	0.56	1.00	2.06	1.93	1.39	0.54	0.48	0.33	0.23

The spin density can be found in 34.7 % on the naphthyl and phenyl groups adjacent to the radical thiazine ring, 18.7 % on one nitrogen atom and only 1.8% on the other nitrogen atom (the one bearing hydrogen), and 44.8 % upon sulfur atoms (deduced value, because the coupling constant with *S* atoms having the low natural ^{33}S abundance could not be seen). The very slow exchange of protons (at the ESR time-scale) between the two nitrogen atoms of the structure has to be mentioned.

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Received on November 4, 1998