ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2012, *57*(4-5), 337-344

Dedicated to Professor Ionel Haiduc
on the occasion of his 75th anniversary

PHENOTHIAZINE-CARBOXALDEHYDE-HYDRAZONE DERIVATIVES SYNTHESIS, CHARACTERIZATION AND ELECTRONIC PROPERTIES

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Received January 31, 2012

Phenothiazine-carboxaldehyde-hydrazones and *bis*-hydrazones were prepared by the microwave assisted condensation of 10-methyl-phenothiazine-3-carboxaldehyde and 10-methyl-phenothiazine-3,7-dicarboxaldehyde respectively, with different substituted hydrazine derivatives in good yields and very short reaction time (3 min). Structural assignments of the new hydrazones were based on mass spectrometry, FT-IR and high resolution NMR spectroscopy analyses; some of the molecular structures were confirmed by X-ray diffraction on single crystals. The electronic properties were examined by absorption/emission UV-Vis spectroscopy and cyclic voltammetry. N,N-Dimethyl-hydrazones show fluorescence in both solution and aggregated state.

INTRODUCTION

Hydrazones are well-known compounds with interesting chemical properties which afforded diverse biological,[1] physical (*i.e.* two-photon materials)[2] or medicinal applications. Hydrazone derivatives with anti-inflammatory, analgesic, anticonvulsant, anti-HIV, antimicrobial,[1] antibacterial,[3] and antitumor properties,[4] pesticide effects (herbicides, insecticides, nematocides, rodenticides) and plant growth regulators activity[4,5] were already reported. Hydrazone derivatives may act as multidentate ligands and their transition metals complexes were already used in the treatment of tuberculosis,[4,6,7] in colorimetric or fluorimetric analytic determinations,[8] as well as in applications involving catalytic processes. Not in the last place, hydrazones are important intermediates in the syntheses of nitrogen containing heterocyclic compounds.[9] Characteristic properties of hydrazones are imprinted by the presence of the >C=N-N< structural unit, which contains two nitrogen atoms with nucleophilic character and a carbon atom which may act as either electrophile or nucleophile according to the reaction environment.[10]

During the last decades, the highly efficient microwave heating became an increasingly popular laboratory technique, especially due to the significant reduction of the reaction time reported for numerous organic reactions.[11]

2,4-Dinitrophenyl hydrazones of phenothiazine carboxaldehyde, were first prepared on analytical purposes, as crystalline derivatives for the characterization of phenothiazine 3-carboxaldehyde and phenothiazine 3,7-*bis*-carboxaldehyde respectively.[12] The aim of this work was to expand the scope of this condensation reaction by synthesizing a series of new hydrazones of phenothiazine carboxaldehydes using differently substituted hydrazine derivatives and taking into consideration both the classical

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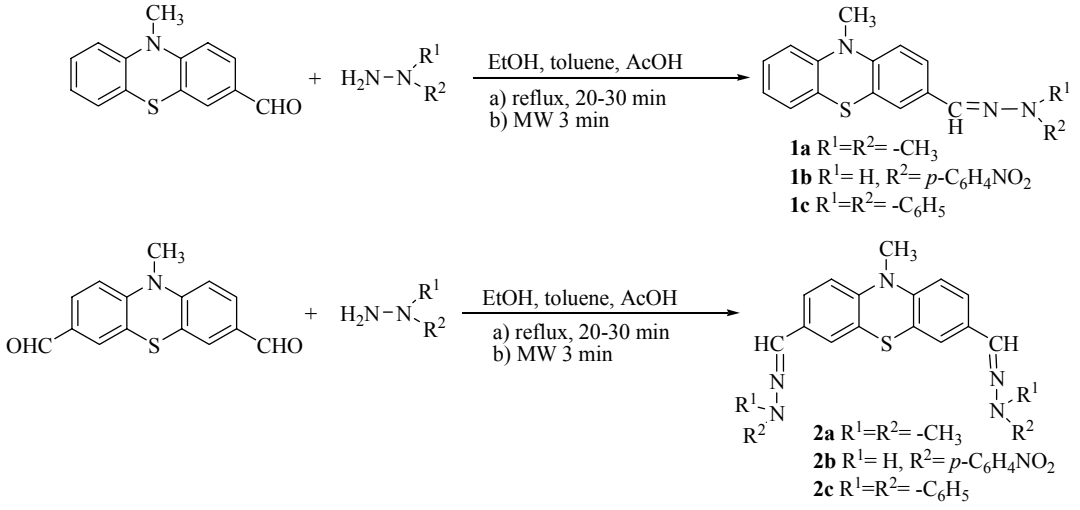
condensation protocols, as well as the modern microwave assisted heating techniques. The structures of the new hydrazones are susceptible for intriguing electronic and coordination properties, due to the existence of an extended π conjugated electron system which combine the heterocyclic phenothiazine core with the >C=N-N< structural unit. Compounds are also susceptible for potential biologic activity suggested by the joint pharmacophore units.

RESULTS AND DISCUSSION

The condensation of 10-methyl-phenothiazine-3-carboxaldehyde with N,N-dimethyl-hydrazine, 4-nitrophenyl-hydrazine and N,N-diphenyl-hydrazine respectively, was performed based on classical condensation protocol,[13] using a reagents ratio of 1:1 and catalytic amounts of acetic acid. Crystalline 10-methyl-phenothiazine-3-carboxaldehyde hydrazones **1a-c** (Scheme 1) were obtained after reflux in toluene-ethanol solution for approximately half an hour. A substantial increase of the reaction rate was observed when the reaction mixtures were alternatively subjected to microwave irradiation in closed reaction vessels. In similar reaction conditions, 10-methyl-phenothiazine-3,7-dicarbaldehyde and the corresponding hydrazine derivative in 1:2 molar ratio gave satisfactory yields of *bis*-hydrazones **2a-c** (Scheme 1), using alternative convective or dielectric heating. Thus, the microwave assisted condensation appears as an advantageous technique affording comparative results in much shorter reaction time.



Scheme 1

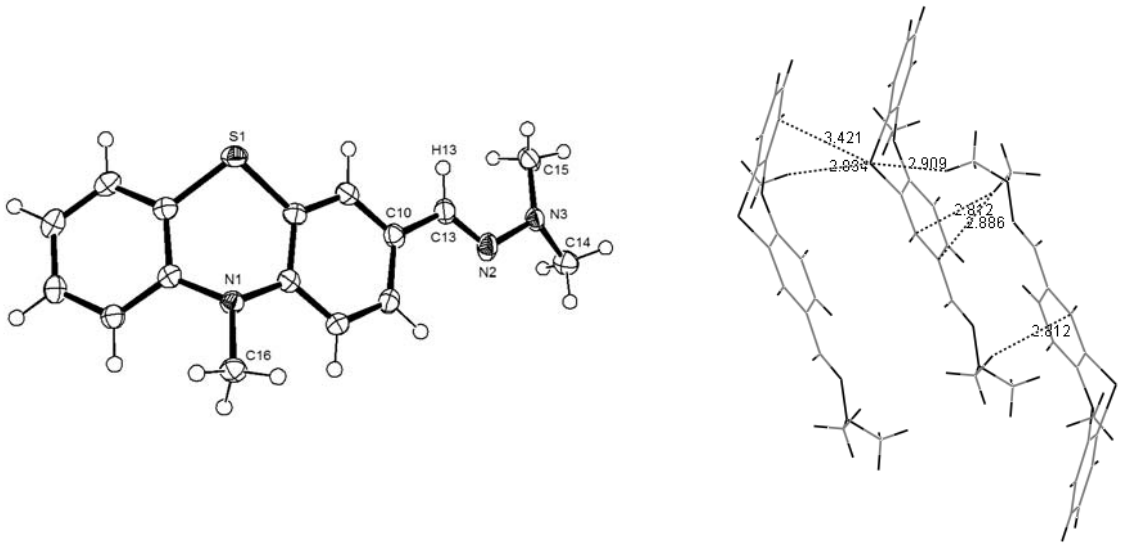


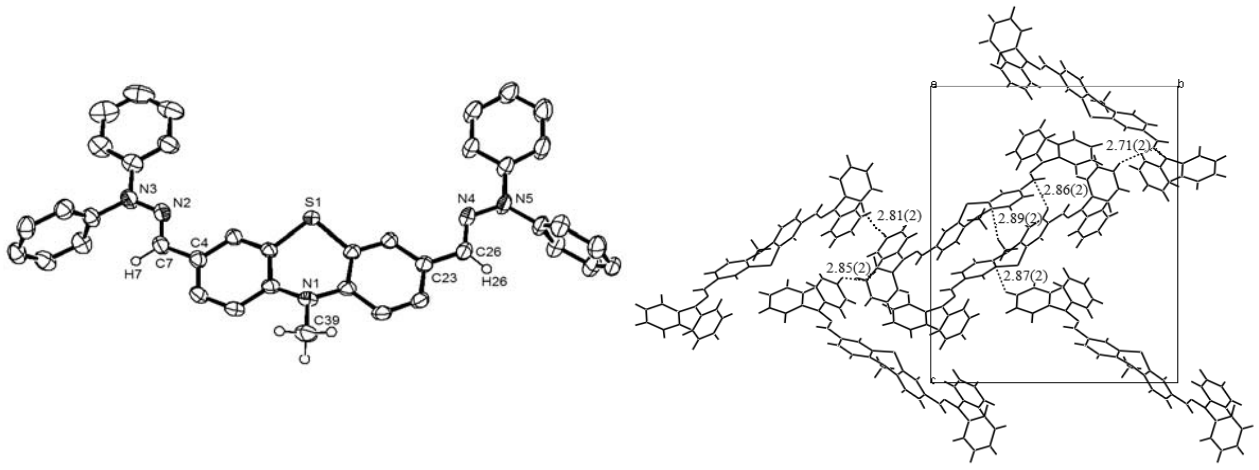
Fig. 1 – Molecular structure of **1a**. a) Ortep plot, b) Supramolecular associations through intermolecular donor acceptor bonds: S(1)···H–C (2.894–2.909 Å), S···C–Ph (3.421 Å) and H···C–Ph (2.812–2.886 Å).

The structure of the hydrazones **1a-c** and *bis*-hydrazones **2a-c** were unambiguously assigned based on recorded ^{1}H–NMR, ^{13}C–NMR, IR and MS spectra. The molecular structures of **1a** and **2c** in the aggregated state were examined by X-ray diffraction on suitable crystals obtained by slow evaporation of an ethanol/acetone/chloroform solution, at room temperature during several weeks.

Compound **1a** (Fig. 1) crystallises in the monoclinic $P2_1/c$ space group with four molecules in the unit cell. The phenotiazine unit is folded about the S–N axis and the large dihedral angle of 162.2° suggests an electron withdrawing effect of the substituent. The N(1)–C(16) bond length of 1.458(2) Å is similar with the N(1)–C(29) distance found in 3,7-Bis(2-pyrid-4'-ylmethylidene-hydrazonoethyl)-(N-ethyl-phenotiazine) (1.454(6) Å).[2] The packing diagram of **1a** shows that the molecules arrange in infinite parallel chains connected through intermolecular donor acceptor bonds as shown in Fig. 1b.

Bis–hydrazone **2c** (Fig. 2) crystallises in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. For each compound **1a** and **2c**, E-configuration at the C=N bond can be observed.

Tables 1 and 2 list the selected bond lengths and angles which are in agreement with reported crystallographic data of 10-alkyl-phenothiazine derivatives.[14]



a **b**

Fig. 2 – Molecular structure of **2c** (Hydrogen atoms on aromatic rings are omitted for clarity). a) Ortep plot, b) Supramolecular associations by π-stacking were detectable as intermolecular donor acceptor bonds: C(11)–H(11)···N(4)#2 (2.71(2) Å), C(39)–H(39C)···C(20)#1 (2.89(2) Å), C(30)–H(30)···C(20)#4 (2.87(2) Å) and C(5)–H(5)···C(26)#1 (2.86(2) Å), C(13)–H(13)···C(17)#3 (2.81(2) Å), C(36)–H(36)···C(12)#5 (2.85(2) Å) (view along a axis).

Table 1

Selected bond lengths (Å) in compounds **1a** and **2c**

1a		**2c**	
S(1)–C(2)	1.763(1)	S(1)–C(21)	1.765(1)
N(1)–C(7)	1.412(1)	N(1)–C(1)	1.404(2)
N(1)–C(1)	1.426(1)	N(1)–C(20)	1.407(2)
N(1)–C(16)	1.458(2)	N(1)–C(39)	1.462(2)
N(2)–C(13)	1.286(2)	N(2)–C(7)	1.282(2)
N(2)–N(3)	1.371(2)	N(2)–N(3)	1.366(2)
N(3)–C(15)	1.450(3)	N(3)–C(14)	1.406(2)
N(3)–C(14)	1.454(3)	N(3)–C(8)	1.438(2)
C(10)–C(13)	1.465(2)	N(4)–C(26)	1.282(2)
		N(4)–N(5)	1.371(2)
		N(5)–C(33)	1.408(2)
		N(5)–C(27)	1.440(2)
		C(4)–C(7)	1.462(2)
		C(23)–C(26)	1.465(2)

Table 2

Selected bond angles (°) in compounds **1a** and **2c**

1a		**2c**	
C(8)–S(1)–C(2)	97.95(5)	C(2)–S(1)–C(21)	99.94(6)
C(7)–N(1)–C(1)	117.41(9)	C(1)–N(1)–C(20)	120.8(1)
C(7)–N(1)–C(16)	118.17(9)	C(1)–N(1)–C(39)	118.7(1)
C(1)–N(1)–C(16)	118.22(9)	C(20)–N(1)–C(39)	118.0(1)
C(13)–N(2)–N(3)	116.6(1)	C(7)–N(2)–N(3)	120.9(1)
N(2)–N(3)–C(15)	121.4(3)	N(2)–N(3)–C(14)	116.2(1)
N(2)–N(3)–C(14)	109.8(3)	N(2)–N(3)–C(8)	121.0(1)
C(15)–N(3)–C(14)	117.0(3)	C(14)–N(3)–C(8)	121.3(1)
N(2)–C(13)–C(10)	120.6(1)	C(26)–N(4)–N(5)	120.0(1)
		N(4)–N(5)–C(33)	116.3(1)
		N(4)–N(5)–C(27)	120.7(1)
		C(33)–N(5)–C(27)	120.5(1)
		N(2)–C(7)–C(4)	118.9(1)
		N(4)–C(26)–C(23)	119.2(1)

The electronic properties of the hydrazones were investigated by absorption/emission UV-Vis spectroscopy and cyclic voltammetry. As it may be seen from Fig. 3a presenting the UV-Vis spectra of representative hydrazones **1a**, **2a** and **2b**, strong absorption bands appear in the UV region due to the electronic transitions involving the molecular orbitals of the phenothiazine chromophore (**1a**, **2a)** and a significant bathochromic shift can be observed for the typical absorption band of **2b** which contains a *p*-nitrophenyl chromophore.

Upon irradiation with UV-Vis absorption maxima, hydrazones **1a** and **2a** show fluorescence emissions, observed in both diluted solutions and solid states. Fig. 3b shows the fluorescence emissions characterized by extremely large Stokes shifts (Table 3). Fluorescence was not observed for the other prepared hydrazones and the explanation lie on the strong face to face π-π stacking interactions between the phenyl units, which are usually responsible for quenching the emission.

Cyclic voltammetry (CV) experiments were carried out on representative compounds **1a** and **2a**, in dichloromethane, using ferrocene/ ferrocenium (Fc/Fc^+) internal standard, with scanning in the anodic (up to 1.5 V) and catodic (up to -0.2V) region. Each compound exhibited two oxidation steps as shown in Fig. 4a,b. In comparison with parent 10-methyl-10*H*-phenothiazine (characterized by the first oxidation potential $E^{0/+1}$=767 mV), the oxidation of hydrazone **1a** occurs at lower potential values ($E_{1/2}{}^{0/+1}$=607 mV), while the oxidation of *bis*-hydrazone **2a** proceeds even easier ($E_{1/2}{}^{0/+1}$=527 mV). The second oxidation peak, which appears at higher oxidation potentials for both compounds (Table 3), appears to be a reversible process in the case of *bis*-hydrazone **2a**.

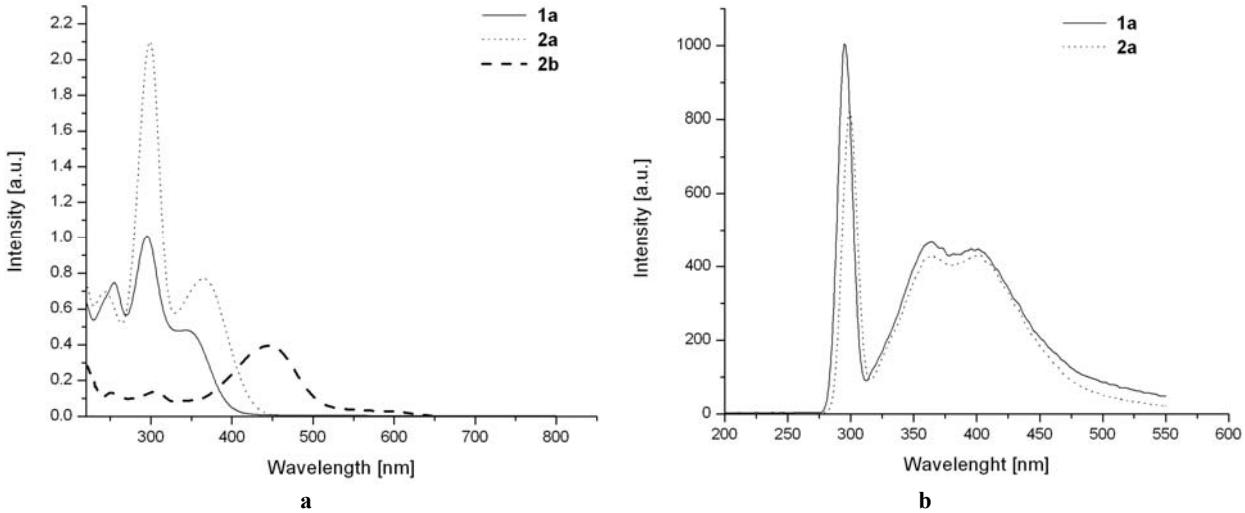


Fig. 3 – a) UV-Vis absorption spectra of hydrazones, 10^{-4}M in acetonitrile.
b) Fluorescence emission spectra of **1a**, **2a** in acetonitrile solution upon excitation at 295 nm.

Table 3

Electronic properties of hydrazones determined by absorption/emission UV-Vis spectroscopy and cyclic voltammetry

Compd.	λ_{abs} (ε_{max}) [nm][a]		λ_{em} [nm][a]	Stokes Shift [cm^{-1}]	$E_{1/2}^{0/+1}$ [V][b]	$E_{1/2}^{+1/+2}$ [V][b]
1a	255 (7560)	**295** (10084)	463	12300	0.607	0.986.
2a	**299** (21030)	365 (7010)	490	13000	0.527	0.879
2b	300 (1310)	435 (5250)	-	-		

[a] solvent: acetonitrile; [b] solvent: chloroform

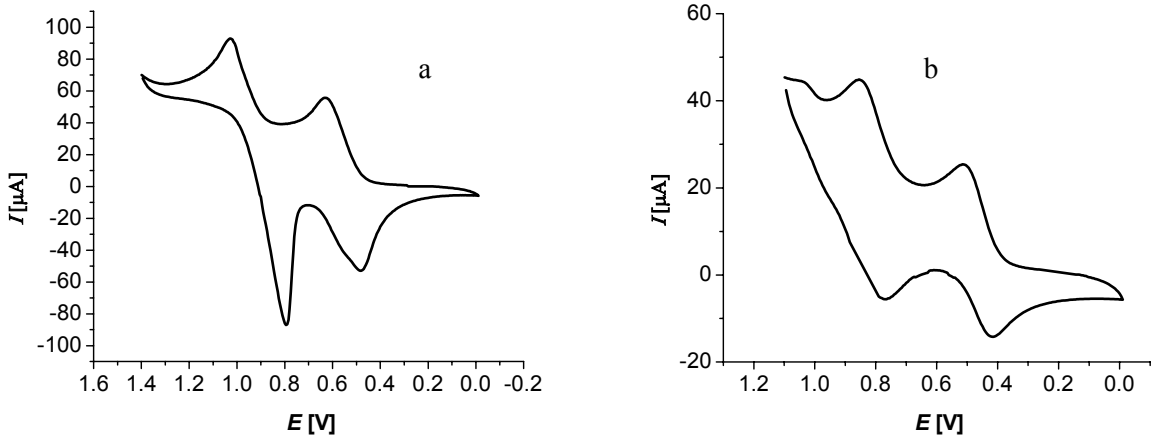


Fig. 4 – Cyclic voltammograms of **1a** (a) and **2a** (b) in CH_2Cl_2, Pt electrode, Ag/AgCl reference, tetra-*n*-butyl ammonium hexafluorophosphate electrolyte, scan rate: 100 $mV \cdot s^{-1}$.

EXPERIMENTAL

3-formyl-10-methyl-phenothiazine and 3,7-diformyl-10-methyl-phenothiazine were obtained according to literature procedures.[15] The hydrazine derivatives were purchased from commercial suppliers.

Microwave assisted syntheses were performed in a CEM Discovery Labmate microwave reactor (300 W power, mono-mode irradiation). ^1H and ^{13}C–NMR spectra were recorded on a Bruker Advance 300 MHz instrument. The infrared spectra were recorded on a Bruker Vector 22 FT-IR spectrometer with scanning between 4000 and 600 cm^{-1}. The mass spectra were recorded on a GS–MS QP 2010 Shimadzu mass spectrometer. The UV-Vis spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer. The fluorescence spectra were recorded on Perkin Elmer LS 55. Thin layer chromatography was performed on Merck DCAlufolien, silica gel 60 F_{254} and components were visualised by UV VL-4LC. The melting points were determined in capillaries with an Electrothermal 9100 instrument. The cyclic voltammetry measurements were performed with a Potentiostat/Galvanostat/ZRA Reference 600. The crystallographic data were collected using a CCD Gemini diffractometer (Agilent Technologies), MoK_α radiation (λ = 0.71073 Å), ω-scan mode. Data reduction was carried out with CrysAlisPro including empirical absorption correction with SCALE3 ABSPACK.[16] The structure was elucidated by direct methods using SHELXS-97 and was refined using SHELXL-97.[17] Non-hydrogen atoms were refined anisotropically. With the exception of the disordered NMe_2 fragment for **1a** all H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. Structure figures were generated with ORTEP.[18] Thermal ellipsoids are drawn at 50% probability if not otherwise mentioned. The relevant crystallographic data and refinement details are shown in Table 4. CCDC 865267 (**1a**) and 865268 (**2c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General procedure for the syntheses of phenothiazine carboxaldehyde hydrazones

a) 10-methyl-phenothiazine carboxaldehyde (2 mmol) was dissolved in toluene (15 ml), absolute ethanol (30 ml), hydrazine derivative (2 mmol) and catalytic amounts of glacial acetic acid were added. In the case of 10-methyl-phenothiazine dicarbaldehyde, the hydrazine derivative in a 1:2 molar ratio was employed. The reaction mixture was heated to reflux under vigorous stirring for 20-30 minutes and then was cooled down at room temperature. The solution was further concentrated *in vacuo* to half volume. The coloured precipitate was filtered, washed with heptane and purified by recrystallisation.

b) 10-methyl-phenothiazine carboxaldehyde (1.2 mmol) was dissolved in toluene (2 ml), absolute ethanol (10 ml), hydrazine derivative (1.4 mmol) and catalytic amounts of glacial acetic acid were added; the reaction mixture was introduced in a reaction tube which was then sealed and subjected to microwaves irradiation for 3 min. at 90 ^oC. In the case of 10-methyl-phenothiazine dicarbaldehyde, the hydrazine derivative in a 1:2 molar ratio was employed. After irradiation the reaction mixture was treated according to method a).

Table 4

Summary of data collections, structure solution and refinement details for **1a** and **2c**

compound	**1a**	**2c**
empirical formula	$C_{16}H_{17}N_3S$	$C_{39}H_{31}N_5S$
fw	283.39	601.75
T, K	130(2)	130(2)
cryst syst	Monoclinic	Orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a, Å	11.7217(3)	7.8557(2)
b, Å	5.6577(1)	17.8668(4)
c, Å	21.6322(4)	23.0287(5)
β, deg.	99.049(2)	90
vol, Å^3	1416.75(5)	3232.2(1)
Z	4	4
$D_{calc,}$ Mg/m^3	1.329	1.237
μ (Mo Kα), mm^{-1}	0.222	0.136
F(000)	600	1264
crystal size, mm^3	0.4 x 0.4 x 0.04	0.4 x 0.4 x 0.3
$\theta_{Min}/\theta_{Max}$, deg.	3.52/ 33.14	2.89/30.51
no of reflns. collected	26738	54572
absolute structure parameter	-	-0.01(5)
no. of indep. reflns.	5391 [R(int) = 0.0310]	9852 [R(int) = 0.0386]
completeness to θ_{Max}, %	99.9	99.9
final R indices [I>2σ(I)]	R_1 = 0.0405 wR_2 = 0.0999	R_1 = 0.0392 wR_2 = 0.0805
R indices (all data)	R_1 = 0.0557 wR_2 = 0.1080	R_1 = 0.0523 wR_2 = 0.0866
goodness-of-fit on F^2	1.029	1.026
largest diff. peak, e·Å^{-3}	0.402 and –0.274	0.195 and –0.196

***3-((2,2-dimethylhydrazono)methyl)-10-methyl-10H-phenothiazine* (1a)**:

The title compound was obtained as a yellow solid (0.5 g, yield: 90%), m.p. = 128–130 °C. IR (ν, cm^{-1}): 2820 w (ν_{C-H}), 1572m ($\nu_{C=N}$), 1497s (ν_{N-CH3}), 1324m (ν_{N-CH3}), 1255s (ν_{C-N}), 1139m (ν_{N-N}), 1034m (ν_{C-S}). EI–MS, *m/z*: 283 (M^+, 100%), 268 (M^+–CH_3, 55%), 238 (7%), 212 (23%). ^{1}H–NMR (300 MHz, $CDCl_3$, δ, ppm): 2.95 (s, 6H, -N(CH_3)$_2$), 3.39 (s, 3H, -N(CH_3)), 6.80 (m, 2H, H_1, H_9, *J*=6.57 Hz), 6.94 (t, 1H, H_7, *J*=7.00 Hz), 7.18 (m, 3H, H_6, H_8, H_b, *J*=7.14 Hz), 7.34 (dd, 1H, H_2, *J*=6.48 Hz), 7.43 (d, 1H, H_4, *J*=1.83 Hz). ^{13}C–NMR (75 MHz, $CDCl_3$, δ, ppm): 35.40 (CH_3), 42.98 (-N(CH_3)$_2$), 113.92 (C_9), 114.01 (C_7), 122.42 (C_3), 123.17 (C_{5a}), 123.59 (C_{4a}), 124.01 (C_2), 125.07 (C_6), 127.15 (C_8), 127.38 (C_4), 131.57 (C_1), 132.37 (C=N), 145.00 (C_{9a}), 145.57 (C_{10a}).

***10-methyl-3-((2-(4-nitrophenyl)hydrazono)methyl)-10H-phenothiazine* (1b):**

1b is a red solid (0.43 g, yield: 95%), m.p. = 261–263 °C. IR (ν, cm^{-1}): 2886w (ν_{C-H}), 1595w ($\nu_{C=N}$), 1560s ($\nu_{N=O}$) 1465w (ν_{N-CH3}), 1280w (ν_{C-N}), 1350s ($\nu_{N=O}$), 1006s (ν_{C-S}). EI–MS, *m/z*: 376 (M^+, 80%), 238 (95%), 223 (100%), 212 (25%), 164 (13%). APCI(+)–MS: 377 (M^++H). ^{1}H–NMR (300 MHz, DMSO-d_6, δ, ppm): 3.34 (s, 3H, -N(CH_3)), 6.98 (m, 3H, $H_{2'}$, $H_{6'}$, H_9), 7.16 (m, 4H, H_1, H_6, H_7, H_8), 7.52 (d, 2H, H_2, H_4, *J*=6.00 Hz), 7.94 (s, 1H, CH=N), 8.11 (d, 2H, $H_{3'}$, $H_{5'}$, *J*=9.00 Hz), 11.24 (s, 1H, NH). ^{13}C–NMR (75 MHz, DMSO-d_6, δ, ppm): 35.78 (CH_3), 111,60 (C_9), 115.20 ($C_{2'}$, $C_{6'}$), 121.97 (C_7), 123.17 ($C_{3'}$, $C_{5'}$), 124.58 (C_{5a}), 126.64 (C_3), 127.05 (C_{4a}), 127.32 (C_2), 128.36 (C_6), 129.65 (C_8), 138.56 (C_4), 141.41 (C_1), 145.04 ($C_{4'}$), 146.47 (CH), 151.02 (C_{9a}), 156.61 (C_{10a}), 184.22 ($C_{1'}$).

***3-((2,2-diphenylhydrazono)methyl)-10-methyl-10H-phenothiazine* (1c):**

The title compound is a dark green solid (0.15 g, yield: 30%), m.p. = 144–146 °C. IR (ν, cm^{-1}): 1589w ($\nu_{C=N}$), 1460w (ν_{N-CH3}), 1236w (ν_{C-N}), 1194w (ν_{N-N}), 907m (ν_{C-H}), 725s (ν_{C-S}). EI–MS, *m/z*: 407 (M^+, 100%), 239 (30%), 212 (80%), 197 (15%), 168 (25%). ^{1}H–NMR (300 MHz, $CDCl_3$, δ, ppm): 3.39 (s, 3H, -N(CH_3)), 6.77 (d, 1H, H_9, *J*=9.00 Hz), 6.84 (d, 1H, H_1, *J*=6.00 Hz), 6.99 (t, 1H, H_7, *J*=6.00 Hz), 7.13 (s, 1H, CH=N), 7.26 (m, 6H, $H_{2'}$, $H_{4'}$, $H_{6'}$, $H_{2''}$, $H_{4''}$, $H_{6''}$), 7.37 (d, 1H, H_2, *J*=6.00 Hz), 7.49 (m, 4H, $H_{3'}$, $H_{5'}$ $H_{3''}$, $H_{5''}$), 7.54 (s, 1H, H_4). ^{13}C–NMR (75 MHz, DMSO-d_6, δ, ppm): 35.49 (CH_3), 113.99 (C_9), 114.22 ($C_{2'}$, $C_{6'}$), 122.57 ($C_{4'}$), 122.64 (C_7), 123.03 (C_{5a}), 123.70 (C_3), 124.50 (C_{4a}), 124.53 (C_2), 125.99 (C_6), 127.23 (C_8), 127.56 ($C_{3'}$, $C_{5'}$), 129.89 (C_4), 130.83 (C_1), 134.73 ($C_{1'}$), 143.75 (CH), 145.40 (C_{9a}), 145.64 (C_{10a}).

***3,7-bis((2,2-dimethylhydrazono)methyl)-10-methyl-10H-phenothiazine* (2a):**

2a is a yellow solid (0.05g, yield: 40%), m.p. = 138–140 °C. IR (ν, cm^{-1}): 2820 w (ν_{C-H}), 2791w, 1572m ($\nu_{C=N}$), 1497s, 1458s (ν_{N-CH3}), 1358m, 1324m (ν_{N-CH3}), 1255s (ν_{C-N}), 1139m (ν_{N-N}), 1034s (ν_{C-S}). EI–MS, *m/z*: 353 (M^+, 100%), 338 (38%), 308 (12%), 282 (25%). ^{1}H–NMR (300 MHz, DMSO-d_6, δ, ppm): 2.51 (s, 12H, -N(CH_3)$_2$), 3.29 (s, 3H, -N(CH_3)), 6.90 (d, 2H, H_1, H_9, *J*=6.00 Hz), 7.22 (d, 2H, H_2, H_8, *J*=6.00 Hz), 7.32 (s, 4H, H_4, H_6, N=CH). ^{13}C–NMR (75 MHz, DMSO-d_6, δ, ppm): 35.41 (CH_3), 42.99 (N-(CH_3)$_2$), 114.03 (C_3, C_7), 122.42

(C_{4a}, C_{5a}), 124.00 (C_2, C_8), 125.09 (C_4, C_6), 127.16 (C_1, C_9), 127.39 (N=C), 145.57 (C_{9a}, C_{10a}).

***10-methyl-3,7-bis((2-(4-nitrophenyl)hydrazono)methyl)-10H-phenothiazine* (2b):**

2b was isolated as dark red solid (0.75 g, yield: 75%), m.p. = 288–290 °C. IR (ν, cm^{-1}): 2818w (ν_{C-H}), 1590s ($\nu_{C=N}$), 1560 ($\nu_{N=O}$), 1495m, 1460s (ν_{N-CH3}), 1350 ($\nu_{N=O}$), 1294s, 1265s (ν_{C-N}), 1128m (ν_{N-N}), 1101s (ν_{C-S}). EI–MS, *m/z*: 539 (M^+, 0.11%), 524 (0.07%), 401 (5.88%), 281 (3.91%). APCI(+)–MS: 540 (M^++H). ^{1}H–NMR (300 MHz, DMSO-d_6, δ, ppm): 3.39 (s, 3H, -N(CH_3)), 6.97 (d, 2H, H_1, H_9, *J*=8.00 Hz), 7.13 (d, 2H, H_2, H_8, *J*=8.00 Hz), 7.20 (d, 4H, H-aryl, *J*=8.90 Hz), 7.52 (s, 2H, H_4, H_6), 7.92 (s, 2H, N=CH), 8.10 (d, 4H, H-aryl, *J*=8.90 Hz), 11.23 (s, 2H, NH).

***3,7-bis((2,2-diphenylhydrazono)methyl)-10-methyl-10H-phenothiazine* (2c):**

The title compound was obtained as a green solid (0.06g, yield: 55%), m.p. = 269 °C. IR (ν_{max}, cm^{-1}): 2818w (ν_{C-H}), 1653w, 1584w ($\nu_{C=N}$), 1559m, 1541m, 1467s (ν_{N-CH3}), 1374m, 1273s (ν_{C-N}), 1217s, 1202s, 1129m (ν_{N-N}), 1087s (ν_{C-S}). EI–MS, *m/z*: 601 (1%), 432 (45%). The NMR spectra could not be recorded because of very low solubility in the deuterated solvents.

CONCLUSIONS

A series of 10-methyl-phenothiazine-carboxaldehyde hydrazones was prepared by the condensation of 10-methyl-phenothiazine-3-carboxaldehyde or 10-methyl-phenothiazine-3,7-dicarboxaldehyde, with N,N-dimethyl-hydrazine, 4-nitrophenyl-hydrazine and N,N-diphenyl-hydrazine respectively. The microwave assisted condensation appeared as a suitable technique affording satisfactory yields in a very short reaction time. The molecular structures, examined by X-ray diffraction in aggregated crystalline state and by high resolution NMR in solution, as well as the electronic properties, determined by UV-Vis absorption spectroscopy and cyclic voltammetry, indicated the typical features of the phenothiazine core moderately tuned by the introduction of the hydrazone unit(s) which increase the typical folding angle of the heterocycle and determines a higher oxidability. N,N-dimethyl-hydrazone **1a** and *bis*-N,N-dimethylhydrazone **2a** show fluorescence emissions characterized by extremely large Stokes shifts in both diluted solution and aggregated state.

Acknowledgments: This work was possible with the financial support of the Sectoral Operational Programme for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project number POSDRU/107/1.5/S/76841 with the title "Modern Doctoral Studies: Internationalization and Interdisciplinarity" (I. A. Torje) and under the project number POSDRU 89/1.5/S/60189 with the title "Postdoctoral Programs for Sustainable Development in a Knowledge Based Society" (A. M. Vălean). Financial support from Ministry of Education, Youth and Sports for grant CAPACITATI III, 33/06.06.08 (SAMPHENO) is also gratefully acknowledged.

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