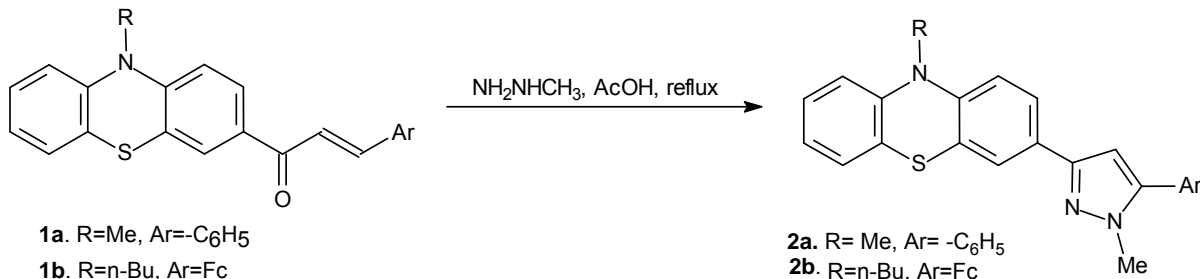


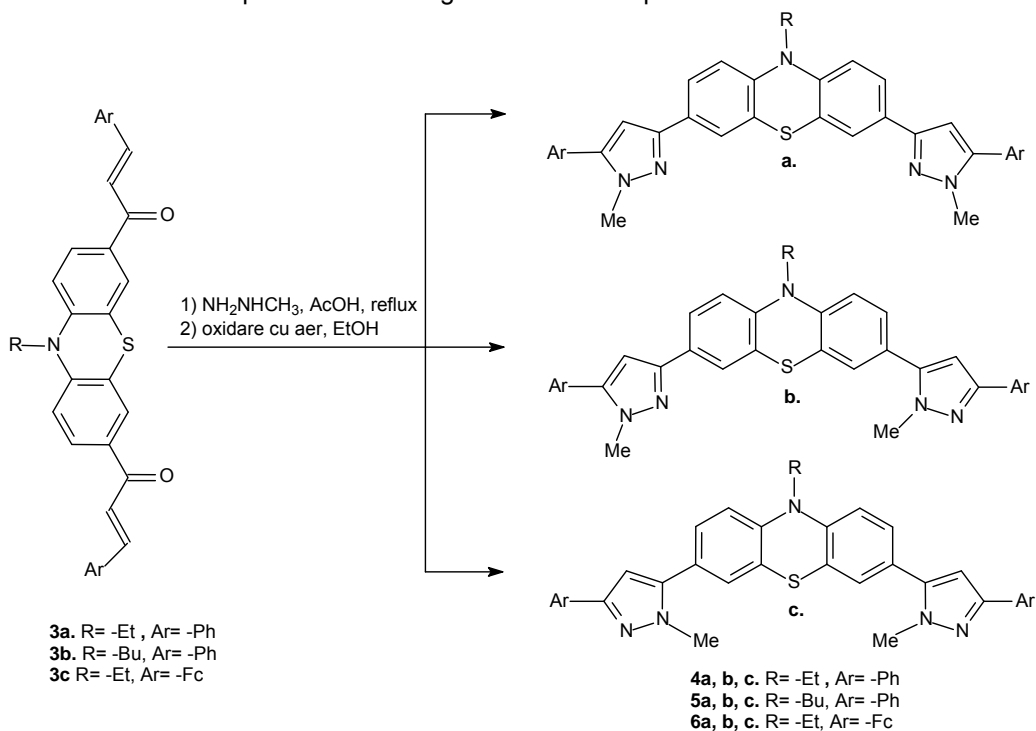
Final report (summary)

In the first part of the Bilateral Project SAMPHENO a series of mono and bis-pyrazolil-phenothiazine derivatives were obtained by substituent dependent regioselective condensation and cyclisation of some mono and bis-chalcones containing phenothiazine units with methylhydrazine. Starting chalcones containing phenothiazine units were synthesized according literature^{1,6,7}. The synthesis of 10-alkyl-3-[1-methyl-5-aryl-1H-pyrazol-3-yl]-10H-phenothiazine (**2a-b**) is presented in scheme 1.



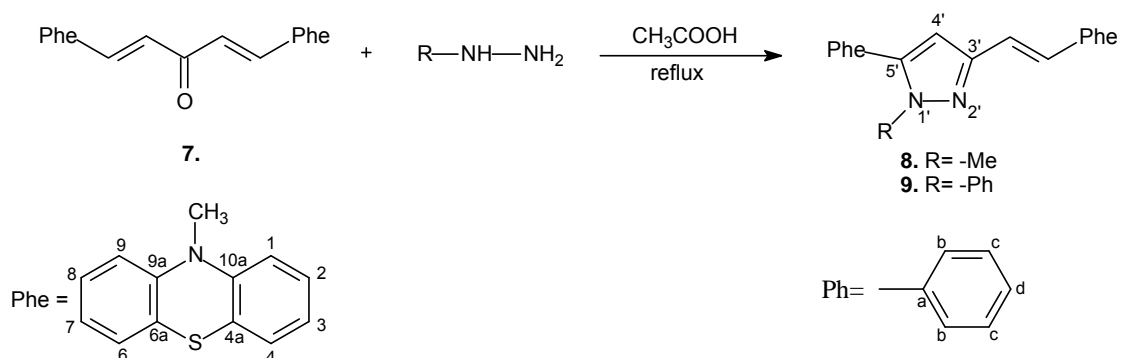
Scheme 1

The syntheses of bis-pyrazoles **4-6** with possible application as bidentate ligands in homogeneous catalysis, were accomplished according to scheme 2. The *ortho* directing properties of the pyrazole rings induce the regioselective metalation of the phenothiazine ring in 4-th and 6-th positions.



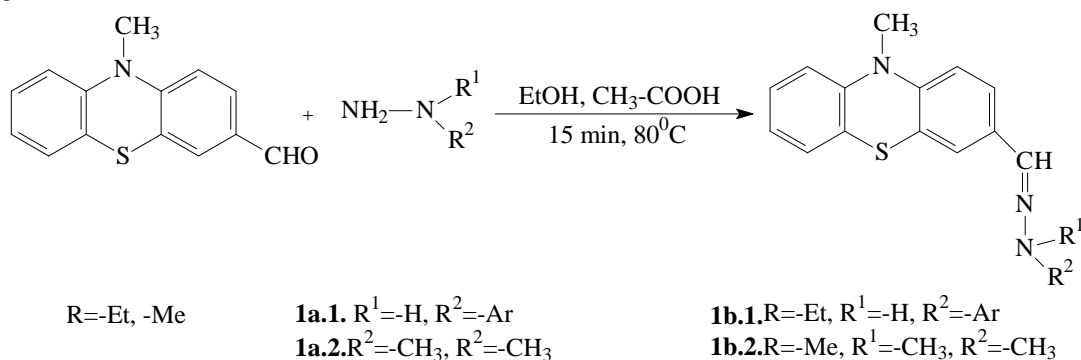
Scheme 2

Other new pyrazoles namely: 10-methyl-3-[(E)vinil-2-(10-metil-3-phenothiazine-3-yl)-5-(10-metil-3-phenothiazine-3-yl)]-1H-pyrazole (**8**) and 10-methyl-3-[(E)vinil-2-(10-metil-3-phenothiazine-3-yl)-5-(10-metil-3-phenothiazine-3-yl)]-1H-pyrazole (**9**) were obtained by the reaction of 1,5-bis-(10-methyl-3-phenothiazin-3-yl)-1,4-pentadien-3-on (**7**) with methyl-hydrazine or phenyl-hydrazine in acetic acid (scheme 3).



Scheme 3

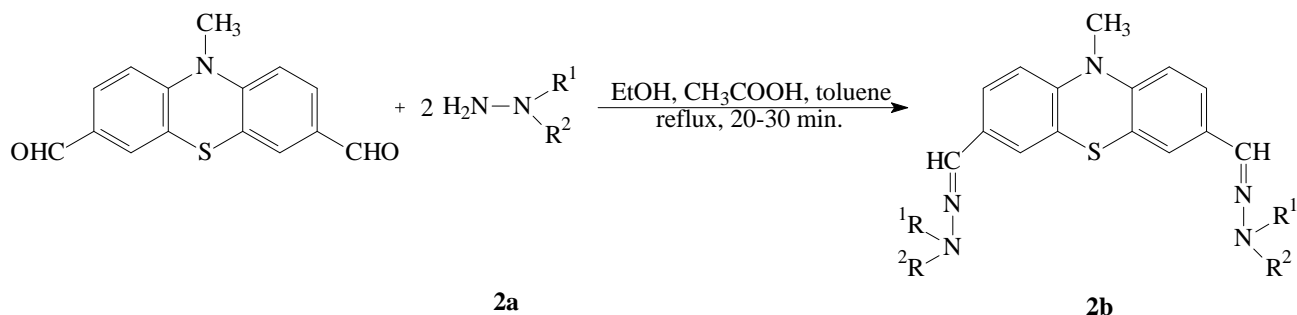
In the second step of this Bilateral Project (Preparation and characterisation of *bis*-hydrazones) mono- and bis-hydrazones were prepared by condensation reaction of some mono- and bis-formyl (and acetyl)-phenothiazine with hydrazine derivatives. The formyl/ acetyl phenothiazine derivatives used as starting materials were obtained according literature^{8,9,10,11,12}. Several mono- and bis-hydrazones, **1b.1-2** were synthesised according to Scheme 4.



Scheme 4

Between the synthesised mono-hydrazones, compounds **1b.1** and **1b.2** are new compounds. Improved procedures were developed for the syntheses of compounds which were previously described in the literature.

The synthesis of bis-hydrazone 3,7-(N,N-dimethyl-hydrizo-methyl)-(10-methyl-10H-phenothiazine) **2b.1**., as well as other derivatives (**2b.2-2b.5**), was performed according to reaction scheme 5:

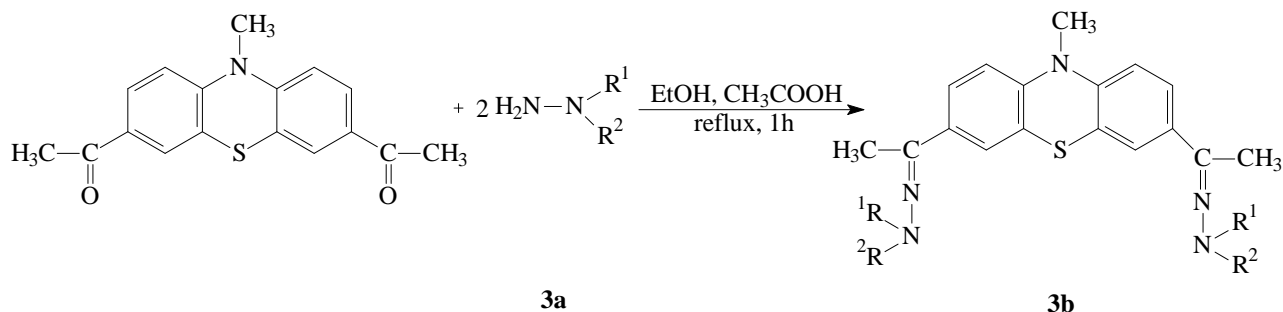


Scheme 5

Table 1. Hydrazine derivatives employed in the reaction with diformyl-phenothiazine derivatives.

No	Reagent (2a)	R ¹	R ²	Product
1	N,N-dimethylhydrazine	-CH ₃	-CH ₃	2b.1./new
2	4-nitro-phenylhydrazine	-H	-C ₆ H ₄ -NO ₂	2b.2./new
3	2,4-dinitro-phenylhydrazine	-H	-C ₆ H ₃ -(NO ₂) ₂	2b.3./new
4	N,N-diphenylhydrazine hydrochloride	-C ₆ H ₅	-C ₆ H ₅	2b.4./new
5	Phenylhydrazine	-H	-C ₆ H ₅	2b.5./new

It was also tested the synthesis of bis-hydrazone-phenothiazine derivatives starting from 3,7-diacetyl-10-alkylphenothiazine (scheme 6). Small reaction yields were obtained because of the lower reactivity of ketone group. We are currently working to optimize reaction conditions.

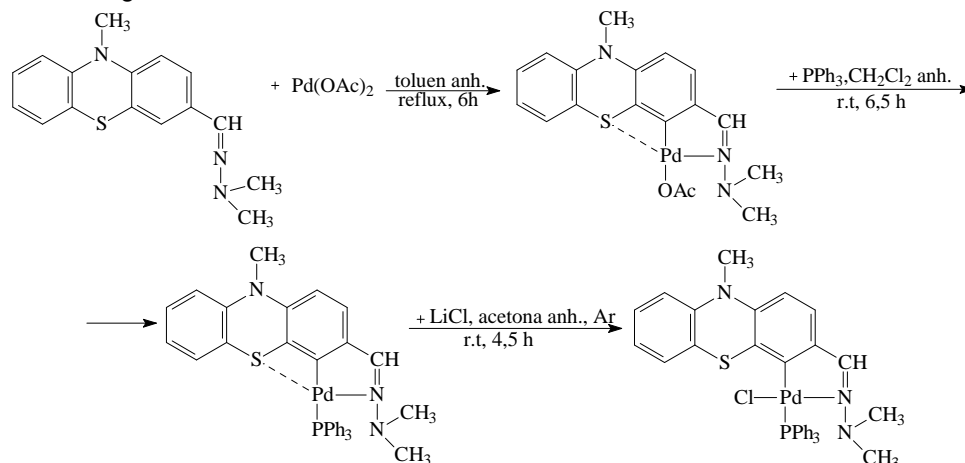


Scheme 6

Table 2. Hydrazine derivatives employed in the reaction with diacetyl-phenothiazine derivatives.

No.	Reagent (3a)	R ¹	R ²	Product
1	Hydrazine	-H	-H	3b.1.
2	Phenylhydrazine	-H	-C ₆ H ₅	3b.2.

The synthesis of palladium organometallic derivative of mono-hydrazone-phenothiazine was accomplished according to Scheme 7:



Scheme 7

The synthesis were carried in inert atmosphere, using Shlenck techniques. The structural characterisation was accomplished by NMR, FT-IR, UV-VIS spectroscopy and Mass Spectrometry.

Conclusions

Under the frame of this Bilateral Project Ro-Hu new mono- and bis-hydrazones, pyrazoles and organometallic derivatives of phenothiazine were succesfully prepared. Molecular modelling calculations were performed in order to predict their stability and electronic proprieties.

New hydrazone-phenothiazine derivatives are fluorescent in day light. Their emission properties were analized by Luminiscence spectroscopy (LS); large Stokes shifts and good cuantic yields were observed. For these reasons the compounds can be recommended for aplications in the field of nonlinear optic materials. Experiments of deposition on solid surfaces are in progress.

Some of the prepared compounds present reversible redox properties and may become suitable mediators for electrochemical processes. These properties are under investigations for the preparation of modified electrodes.

As a result of joint research activities carried under the frame of this Bilateral Project, one scientific article was published in *Journal of Organometallic Chemistry*, and one manuscript was prepared for submission to a journal which will be selected by the Romanian authors.

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