

SYNTHESIS AND FLUORESCENCE PROPERTIES OF NEW SCHIFF BASES CONTAINING PHENOTHIAZINE UNITS

EMESE GÁL^a, LUIZA GĂINĂ^a, TAMÁS LOVÁSZ^a, CASTELIA CRISTEA^a
AND LUMINIȚA SILAGHI-DUMITRESCU^a

ABSTRACT. New heterocyclic Schiff bases exhibiting fluorescent properties were obtained in good yields by thermal condensation of (10-alkyl)-3-formyl-10H-phenothiazine derivatives with aromatic amines. Structural characterization was based on high resolution NMR, UV-Vis and fluorescence spectroscopy. Emission maxima were situated in the range 524-588 nm showing large Stokes shifts.

Keywords: Schiff bases, formylphenothiazine, fluorescence spectroscopy.

INTRODUCTION

Schiff bases characterized by diverse structural properties can be obtained by relatively simple preparation procedures based on condensation reaction of aromatic amines and carbonyl derivatives [1] This synthetic flexibility enabled the design of molecular structures with tuneable properties and numerous representative derivatives found a wide variety of applications in many fields such as biology (due to similarities with natural biological compounds [2] analytical chemistry (optical, electrochemical, and chromatographic sensors) [3,4] and materials chemistry (e.g. due to electroluminescent properties required in *light emitting diodes* OLED, PLED)

Successful application of Schiff bases requires a careful study of their characteristics because many of these azomethines are chemically unstable and show a pronounced tendency to be involved in tautomeric equilibria, hydrolysis, or formation of ionized species [5]

Schiff bases containing phenothiazine units were obtained either by condensation of N-alkyl-3-aminophenothiazine derivatives with benzaldehyde derivatives [6,7], or by condensation of N-alkyl-3-formylphenothiazine derivatives with aromatic primary amines such as aniline [8], aminobenzoic acid derivatives [9] and 5-amino-1-phenyl-pyrazol derivatives [10]. Previous studies regarding the preparation of *bis*-Schiff bases containing phenothiazine units indicate also two alternative synthetic routes, the condensation of N-alkyl-3-formylphenothiazine derivatives with aliphatic or aromatic diamines [10,11] as well as condensation

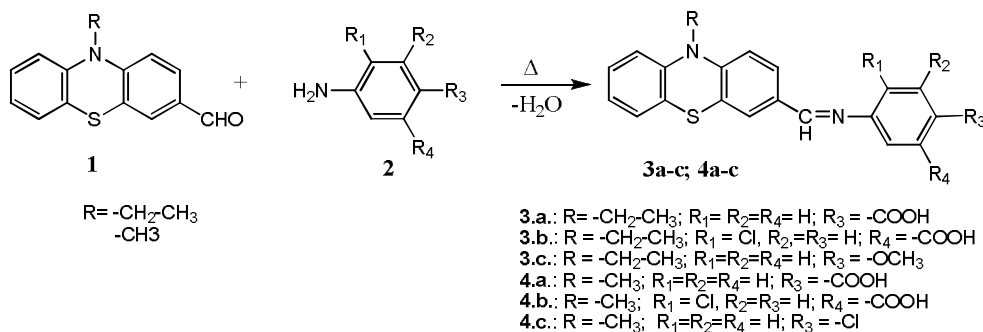
^a Universitatea Babeș-Bolyai, Facultatea de Chimie și Inginerie Chimică, Str. Kogălniceanu, Nr. 1, RO-400084 Cluj-Napoca, Romania, castelia@chem.ubbcluj.ro

of N-alkyl-3,7-diformylphenothiazine with amines [12]. Polyazomethine-type conjugated polymers with alternating phenothiazine (PZ) and azomethine units ($-C=N-$), were synthesized and their electroluminescent properties were studied from the viewpoint of polymer structure vs. emission color and efficiency. Single- and double-layer *polymer light-emitting diode* PLEDs were fabricated [13]. The conjugated copolymer, poly[N-(2-ethylhexyl)phenothiazine-alt-6-Ph phenanthridine] [poly(PZ-PTI)], with azomethine linkages, was also synthesized by a Schiff-base reaction. Single-layered and double-layered PLED made with poly(PZ-PTI) as an emitting layer were fabricated and exhibited EL (emission) at 572 nm [14].

The aim of this work is to add new data to our previous reports, by describing the synthesis and structural characterization of new Schiff bases containing phenothiazine units and to emphasize their electroluminescent properties by fluorescence spectroscopy.

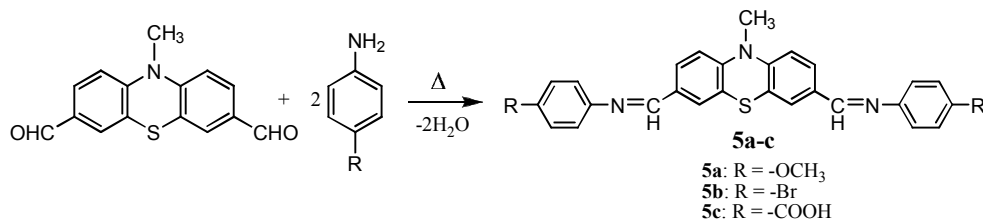
RESULTS AND DISCUSSION

A series of new Schiff bases **3-4** were obtained by the condensation of 10-alkyl-3-formylphenothiazine **1** with aniline/*p*-aminobenzoic acid derivatives **2** as shown in scheme 1.



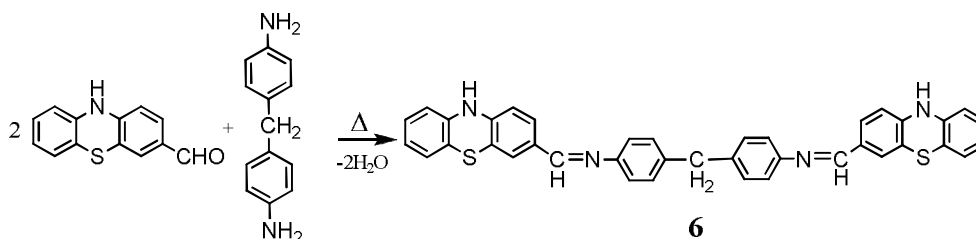
Scheme 1

Similar conditions consisting of heating the reaction mixture to reflux in ethanol solution, were applied for the condensation of 10-alkyl-3,7-diformylphenothiazine with aniline/*p*-aminobenzoic acid derivatives leading to *bis*-Schiff bases **5a-c** (scheme 2).



Scheme 2

Bis-Schiff base **6** was obtained in good yields by the condensation of 3-formyl-10*H*-phenothiazine [15] with *p,p'*-diamino diphenylmethane (scheme 3). Due to unsubstituted NH group in the heterocycle unit, oxidation occurs easily in the presence of air.



Scheme 3

The structure assignment of new Schiff bases **3-6** is supported by spectroscopic data. EI mass spectra revealed the corresponding molecular peaks. In particular, azomethine group can be clearly identified by the appearance of the characteristic proton and carbon resonances in NMR spectra, as a deshielded singlet signal situated at 8.3-8.5 ppm in the ^1H -NMR spectra and a signal situated at 153-160 ppm in the ^{13}C -NMR spectra.

The absorption of the *e.m.* radiation in the UV-Vis domain generated electronic spectra with characteristic maxima presented in table 1 for both starting materials (3-formyl-phenothiazine derivatives) and new Schiff bases. All Schiff bases **3-6** contain the same cromophor unit consisting of an extended π conjugated system containing phenothiazinyl and phenyl aromatic units linked by an azomethine group and thus, very similar absorption maxima were recorded in the UV spectra. However, a small bathochromic shift can be noticed for lowest energy absorption maxima of *bis*-Schiff bases **5** as compared to mono Schiff bases **3-4**.

As expected, substitution of the heterocyclic nitrogen atom does not exert great influence upon the position of the absorption maxima. Small shifts can be correlated with the nature of auxochrome groups attached in position *meta* or *para* of the phenyl units.

The emission spectra of Schiff bases **3-6** contain broad bands in the range 525-588 nm with large Stokes shifts ($6000\text{-}8600\text{ cm}^{-1}$) as shown in Table 1.

The Schiff bases **3a** and **4a** are characterized by lower energy emission maxima ($\lambda_{\text{max, em}}$ 588 nm and 583 nm respectively) as compared to *bis*-Schiff base **5c** ($\lambda_{\text{max, em}}$ 535 nm). Meanwhile, the smallest Stokes shifts were observed for *bis*-Schiff bases **5** ($5800\text{-}6100\text{ cm}^{-1}$), a fact in agreement with literature data stating that great Stokes shifts can be assigned to large geometrical changes upon excitation from nonplanar ground state to a essentially planarized excited state [16].

Table 1. Electronic properties of Schiff base determined by UV-Vis and LE spectroscopy in THF

Compound	Absorption $\lambda_{\max, \text{abs}}$ [nm]	Emission $\lambda_{\max, \text{em}}$ [nm]	Stokes shift (cm^{-1})
3.a.	243, 278, 392	588	8500
3.b.	245, 279, 389	572	8200
3.c.	236, 273, 379	528	7400
4.a.	243, 275, 388	583	8600
4.b.	244, 285, 381	554	8200
4.c.	239, 275, 380	545	8000
5.a.	234, 290, 401	524	5800
5.b.	241, 298, 411^a	546	5900
5.c.	287, 404	535	6100
6.	244, 294, 399^a	525	6000
10-Me-3-formyl-phenothiazine	286, 377^a	525	7500
10-Et-3-formyl-phenothiazine	294, 381^a	528	7300
10 <i>H</i> -3-formyl-phenothiazine	292, 393^a	523	6300
10-Me-3,7-diformyl-phenothiazine	284, 394^a	521	6200

^a-the UV-Vis, and Fluorescence spectra were recorded in ACN

CONCLUSIONS

Thermal condensation of (10-alkyl)-3-formyl-10*H*-phenothiazine derivatives with aromatic amines generate heterocyclic Schiff bases characterized by green-yellow fluorescence. The exhibited emission maxima were situated in the range 524-588 nm showing large Stokes shifts ($6000\text{-}8500\text{ cm}^{-1}$), thus recommending these compounds for possible applications in nonlinear optical materials.

EXPERIMENTAL SECTION

FT-IR spectrometer Bruker Vector 22; 300 MHz NMR spectrometer Bruker; UV-Vis spectrometer Perkin Elmer Lambda 35; Luminescence Spectrometer Perkin Elmer LS 55; EI MS Shimadzu QP 2010; Merck reagents.

4-((10-ethyl-10*H*-phenothiazin-3-yl)-methylenamino)benzoic acid **3.a.**

3-Formyl-10-ethyl-phenothiazine 0.5g (1.9mmol) and p-amino-benzoic acid 0.268g (1.9mmol) were refluxed in ethanol for 24 hours. After solvent evaporation an orange powder product with melting point 249°C was obtained in 80% yield.

MS (EI) m/z = 374 (63%) M^{+} .

¹H NMR, 400 MHz, DMSO- d_6 : $-\text{CH}_2$ δ = 3.98 ppm (q, 3J = 6.80 Hz, 2H) $-\text{CH}_2$; δ = 1.34 ppm (t, 3J = 6.8 Hz, 3H) $-\text{CH}_3$; δ = 7.13 ppm, (d, 3J = 8.8 Hz, 1H) H_1 ; δ = 7.75 ppm, (d, 3J = 8.8 Hz, 1H) H_2 ; δ = 8.50 ppm, (s, 1H) $\text{CH}=\text{N}$; δ = 7.67 ppm, (s, 1H) H_4 ; δ = 7.07 ppm, (d, 3J = 8 Hz, 1H) H_6 ; δ = 6.98 ppm, (t, 3J = 8 Hz, 1H) H_7 ; δ = 7.22 ppm, (t, 3J = 7.6 Hz, 1H) H_8 ; δ = 7.16 ppm, (d, 3J = 7.6 Hz, 1H) H_9 ; δ = 7.97 ppm, (d, 3J = 8.4 Hz, 2H) $\text{H}_{2',6'}$; δ = 7.29 ppm, (d, 3J = 8.4 Hz, 2H) $\text{H}_{3',5'}$; δ = 12.85 ppm, (s, 1H) $-\text{COOH}$.

¹³C NMR, DMSO-*d*₆: δ ppm 12.5 (-CH₂), 41.5 (-CH₃), 127.1 (C₁), 129.3 (C₂), 130.1 (C₃), 126.8 (C₄), 124.6 (C_{4a}), 122.8 (C_{5a}), 115.8 (C₆), 123.1 (C₇), 127.9 (C₈), 115.2 (C₉), 143.1 (C_{9a}), 160.6 (CH=N), 155.5 (C_{1'}), 130.5 (C_{2',6'}), 121 (C_{3'5'}), 121.9 (C_{4'}), 167.2 (COOH).

4-Chloro-3-((10-ethyl-10H-phenothiazin-3-yl)methyleneamino)benzoic acid 3.b.

3-formyl-10-ethyl-phenothiazine 0.5g (1.9mmol) and 3-amino-4-chloro-benzoic acid 0.266g (1.9mmol) were stirred at 78°C for 24 hours in isoamyl-alcohol. The product was purified by recrystallization from ethyl acetate. A light green coloured solid precipitate, with melting point 209°C, was collected by filtration. Yield 50%.

MS: m/z= 408/410(73%) M⁺.

¹H NMR, 400 MHz, DMSO-*d*₆: δ= 3.97 ppm (q, ³J=7 Hz, 2H) CH₂; δ= 1.33 ppm (t, ³J=7 Hz, 3H) CH₃; δ= 7.14 ppm, (d, ³J=8.4 Hz, 1H) H₁; δ= 7.79 ppm, (d, ³J=8.4 Hz, 1H) H₂; δ=8.51 ppm, (s, 1H) CH=N; δ=7.69 ppm, (s, 1H) H₄; δ=7.05 ppm, (d, ³J=8.4 Hz, 1H) H₆; δ=6.98 ppm, (dd, ³J=8.4 Hz, ³J=8 Hz, 1H) H₇; δ= 7.21 ppm, (dd, ³J= 9.2 Hz, ³J=8 Hz, 1H) H₈; δ=7.12 ppm, (d, ³J= 9.2 Hz, 1H) H₉; δ= 7.71 ppm (s, 1H) H₂; δ= 7.76 ppm, (d, ³J= 8.4 Hz, 1H) H₆; δ= 7.63 ppm, (d, ³J= 8.4 Hz, 1H) H₅.

¹³C NMR, DMSO-*d*₆: δ ppm: 12.2 (-CH₂), 41.5 (-CH₃), 126.7 (C₁), 129.2 (C₂), 130.6 (C₃), 161.5 (C=N), 129.9 (C₄), 127.3 (C_{4a}), 122.6 (C_{5a}), 115.8 (C₆), 122.9 (C₇), 126.8 (C₈), 115.6 (C₉), 142.8 (C_{9a}), 144.8 (C_{10a}), 148.6 (C_{3'}), 127.3 (C_{4'}), 120.4 (C_{5'}), 121.7 (C_{6'}), 131.8 (C_{1'}), 147.2 (C_{2'}), 166.2 (COOH).

4-methoxy-N-((10-ethyl-10H-phenothiazin-3-yl)methylene)aniline 3.c.

3-formyl-10-ethyl-phenothiazine 0.5g (1.9mmol) and p-methoxy-aniline 0.246g (2.1mmol) were refluxed in ethyl alcohol for 24 hours. The product was purified by recrystallization from ethanol. A lemon-yellow coloured solid precipitate was collected by filtration, with melting point 108°C. Yield 76%.

MS: m/z= 360 (76%) M⁺.

¹H NMR, 400 MHz, DMSO-*d*₆: δ= 3.93 ppm (q, ³J=7 Hz 2H) -CH₂; δ= 1.41 ppm (t, ³J=7 Hz 3H) CH₃; δ= 6.86 ppm, (d, ³J= 8.40 Hz, 1H), H₁; δ= 7.58 ppm, (d, ³J= 8.40 Hz, 1H) H₂; δ=8.30 ppm, (s, 1H) CH=N; δ=7.63 ppm, (s, 1H) H₄; δ=7.09 ppm, (d, ³J= 8 Hz 1H) H₆; δ=6.91 ppm, (t, ³J= 8 Hz, 1H) H₇; δ= 7.58 ppm, (t, ³J= 8 Hz, 1H) H₈; δ= 6.84 ppm, (d, ³J= 8.4 Hz 1H) H₉; δ= 6.90 ppm (d, ³J= 8.8 Hz, 2H) H_{2',6'}; δ= 7.18 ppm, (d, ³J= 8.8 Hz, 2H) H_{3',5'}.

¹³C NMR, DMSO-*d*₆ δ ppm: 12.9 (CH₂), 42.1 (CH₃), 55.4 (OCH₃), 114.6 (C₁), 128.3 (C₂), 130.9 (C₃), 153.8 (C=N), 126.9 (C₄), 124.4 (C_{4a}), 123.6 (C_{5a}), 127.3 (C₆), 122.8 (C₇), 127.3 (C₈), 115.2 (C₉), 143.8 (C_{9a}), 147.2 (C_{10a}), 144.9 (C_{1'}), δ= 114.3 (C_{2',6'}), 122.1 (C_{3',5'}), 158.0 (C₄).

4-((10-methyl-10H-phenothiazin-3-yl)-methylenamino)benzoic acid 4.a.

3-formyl-10-methyl-phenothiazine 0.5g (2.0mmol) and p-amino-benzoic acid 0.28g (2.0mmol) were refluxed in ethyl alcohol for 24 hours. The product was purified by recrystallization from toluene. After filtration an orange yellow coloured solid precipitate was collected by filtration, with melting point 256°C. Yield 70%.

MS: m/z= 360 (68%) M⁺.

¹H NMR, 400 MHz, DMSO-*d*₆: δ= 3.5 ppm (s, 3H) CH₃; δ= 6.99 ppm, (d, ³J= 5.2 Hz, 1H) H₁; δ= 7.71 ppm, (d, ³J= 5.2 Hz, 1H) H₂; δ=8.51 ppm, (s, 1H) CH=N; δ=7.70 ppm (s, 1H) H₄; δ=7.19 ppm, (d, ³J= 6.4 Hz, 1H) H₆; δ=7.03 ppm, (dd, ³J= 6.4 Hz,

$^3J = 8.2$ Hz, 1H) H_7 ; $\delta = 7.24$ ppm, (t, $^3J = 8.2$ Hz, $^3J = 7.6$ Hz, 1H) H_8 ; $\delta = 7.02$ ppm, (d, $^3J = 7.6$ Hz, 1H) H_9 ; $\delta = 7.26$ ppm, (d, $^3J = 8.4$ Hz, 2H), $H_{3',5'}$; $\delta = 7.98$ ppm, (d, $^3J = 8.4$ Hz, 2H) $H_{2',6'}$; $\delta = 9.80$ ppm, (s, 1H) -COOH.

^{13}C NMR, DMSO- d_6 δ ppm: 35.5 (-CH₃), 114.6 (C₁), 159.5 (C=N), 126.8 (C₄), 126.5 (C_{4a}), 126.9 (C₆), 129.5 (C₇), 121.2 (C₈), 142.5 (C_{9a}), 144.8 (C_{10a}), 118.4 (C_{5a}), 155.5 (C_{1'}), 130.5 (C_{2',6'}), 121 (C_{3'5'}), 121.9 (C_{4'}), 167 (COOH).

4-chloro-3-((10-methyl-10H-phenothiazin-3-yl)methyleneamino)benzoic acid 4.b.

3-formyl-10-methyl-phenothiazine 0.5g (2.0mmol) and 3-amino-4-chloro-benzoic acid 0.53g (2.0mmol) were heated at 78°C in isoamyl -alcohol under stirring for 24 hours. The product was purified by recrystallization from ethyl acetate. After filtration an orange yellow coloured solid precipitate was collected by filtration, with melting point 243-244°C. Yield 80%.

MS: $m/z = 394/396$ (72%) M^+

^1H NMR, 300 MHz, DMSO- d_6 : $\delta = 3.38$ ppm (s, 3H) -CH₃; $\delta = 7.02$ ppm, (d, $^3J = 7.8$ Hz, 1H) H_1 ; $\delta = 7.81$ ppm, (d, $^3J = 7.8$ Hz, 1H) H_2 ; $\delta = 8.51$ ppm, (s, 1H) CH=N; $\delta = 7.70$ ppm, (s, 1H) H_4 ; $\delta = 7.19$ ppm, (d, $^3J = 8.1$ Hz, 1H) H_6 ; $\delta = 6.99$ ppm, (t, $^3J = 8$ Hz, 1H) H_7 ; $\delta = 7.24$ ppm, (t, $^3J = 8$ Hz, 1H) H_8 ; $\delta = 7.08$ ppm, (d, $^3J = 8.4$ Hz, 1H) H_9 ; $\delta = 7.60$ ppm, (d, $^3J = 8.1$ Hz, 1H) H_5 ; $\delta = 7.76$ ppm, (d, $^3J = 8.1$ Hz, 1H) H_6 ; $\delta = 7.73$ ppm, (s, 1H) $H_{2'}$.

4-Chloro-N-((10-methyl-10H-phenothiazin-3-yl)methylene)aniline 4.c.

3-formyl-10-methyl-phenothiazine 1g (4.14mmol) and 4-chloroaniline 0.53g (4.14mmol) were refluxed in ethanol for 6 hours. After filtration an orange yellow coloured solid precipitate with melting point 125°C was collected. Yield 98%.

MS $m/z = 349/401$ (100%) M^+

^1H NMR, 300 MHz, CDCl₃: $\delta = 3.42$ ppm (s, 3H) CH₃; $\delta = 6.82$ ppm (d, $^3J = 8.4$ Hz, 1H) H_1 ; $\delta = 7.63$ ppm (d, $^3J = 8.4$ Hz, 1H) H_2 ; $\delta = 8.29$ ppm (s, 1H) CH=N; $\delta = 7.70$ ppm, (s, 1H) H_4 ; $\delta = 7.22$ ppm (d, $^3J = 7.0$ Hz, 1H) H_6 ; $\delta = 6.98$ ppm, (t, $^3J = 7.2$ Hz, 1H) H_7 ; $\delta = 7.23$ ppm (t, $^3J = 7.2$ Hz, 1H) H_8 ; $\delta = 6.85$ ppm (d, $^3J = 8.4$ Hz, 1H) H_9 ; $\delta = 7.35$ ppm (d, $^3J = 8.6$ Hz, 2H) $H_{2',6'}$; $\delta = 7.14$ ppm, (d, $^3J = 8.6$ Hz, 2H) $H_{3',5'}$.

^{13}C NMR, CDCl₃ δ ppm: 35.6 (-CH₃), 126.9 (C₁), 129.1 (C₂), 130.5 (C₃), 159.2 (C=N), $\delta = 129.2$ (C₄), 122.7 (C_{5a}), 114.5 (C₆), 123.1 (C₇), 123.9 (C₈), 114.5 (C₉), 144.7 (C_{9a}), 144.8 (C_{10a}), 118.5 (C_{4a}), 148.6 (C₁'), 127.2 (C_{2',6'}), 122.2 (C_{3'5'}), 150.6 (C_{4'}).

***N,N'*-((10-methyl-10H-phenothiazine-3,7-diyl)bis(methan-1yl-1-ylidene))bis(4-methoxyaniline) 5.a.**

3,7-diformyl-10-methyl-phenothiazine 0.5g (1.86mmol) and 4-methoxy-aniline 0.45g (3.7mmol) were refluxed in ethanol under stirring for 16 hours. After filtration an orange yellow coloured solid was obtained, melting point 234°C. Yield 68%.

MS $m/z = 479$ (100%) M^+

^1H NMR, 300 MHz, CDCl₃: $\delta = 3.47$ ppm (s, 3H) CH₃; OCH₃ $\delta = 3.85$ ppm, (s, 6H); $\delta = 6.86$ ppm, (d, $^3J = 8.4$ Hz, 2H) $H_{1,9}$; $\delta = 7.64$ ppm, (d, $^3J = 8.4$ Hz, 2H) $H_{2,8}$; $\delta = 8.36$ ppm, (s, 2H) CH=N; $\delta = 7.71$ ppm, (s, 2H) $H_{4,6}$; $\delta = 6.94$ ppm, (d, $^3J = 8.8$ Hz, 4H) $H_{2'2'',6'6''}$; $\delta = 7.23$ ppm, (d, $^3J = 8.8$ Hz, 4H) $H_{3'3'',5'5''}$.

^{13}C NMR, CDCl₃ δ (ppm): 35.9 (-CH₃), 55.5 (-OCH₃); 126.7 (C_{1,9}), 128.7 (C_{2,8}), 131.6 (C_{3,7}), 158.1 (C=N), 122.2 (C_{4,6}), 124.4 (C_{4a,5a}), 147.2 (C_{9a,10a}), 114.8 (C_{2'2'',6'6''}), 148.1 (C_{1'1''}), 124.8 (C_{3'3'',5'5''}), 156.7 (C_{4'4''}).

***N,N'*-(10-methyl-10*H*-phenothiazine-3,7-diyl)bis(methan-1yl-1-ylidene)bis(4-bromoaniline) 5.b.**

3,7-diformyl-10-methyl-phenothiazine 0.5g (1.86mmol) and 4-bromoaniline 0.64g (3.72mmol) were refluxed in ethanol was stirred for 10 hours at 78°C.. After filtration an orange yellow coloured solid precipitate was obtained, with melting point 222-224°C. Yield 58%.

MS m/z = 575/577/579 (100%) M^+ .

$^1\text{H NMR}$, 300 MHz, CDCl_3 : δ = 3.49 ppm (s, 3H) CH_3 ; δ = 6.88 ppm, (d, 3J = 8.4 Hz, 2H) $\text{H}_{1,9}$; δ = 7.65 ppm, (d, 3J = 8.4 Hz, 2H) $\text{H}_{2,8}$; δ = 8.31 ppm, (s, 2H) $\text{CH}=\text{N}$; δ = 7.72 ppm, (s, 2H) $\text{H}_{4,6}$; δ = 7.51 ppm, (d, 3J = 8.6 Hz, 4H) $\text{H}_{2',2''6'6''}$; δ = 7.09 ppm, (d, 3J = 8.6 Hz, 4H) $\text{H}_{3'3''5'5''}$.

$^{13}\text{C NMR}$, CDCl_3 δ (ppm): 30.9 ($-\text{CH}_3$); 126.9 ($\text{C}_{1,9}$), 129.2 ($\text{C}_{2,8}$), 131.2 ($\text{C}_{3,7}$), 158.9 ($\text{C}=\text{N}$), 122.6 ($\text{C}_{4,6}$), 118.2 ($\text{C}_{4a,5a}$) 144.8 ($\text{C}_{9a,10a}$) 114.8 ($\text{C}_{2'2'',6'6''}$), 147.5 ($\text{C}_{1'1''}$), 124.8 ($\text{C}_{3'3'',5'5''}$), 122.3 ($\text{C}_{4'4''}$).

***4,4'*-(10-methyl-10*H*-phenothiazine-3,7-diyl)bis(methan-1yl-1-ylidene)bis(aza-1-yl-1-ylidene)dibenzoic acid 5.c.**

3,7-diformyl-10-methyl-phenothiazine 0.39g (1.4mmol) and *p*-amino-benzoic acid 0.39g (2.8mmol) in ethyl alcohol was refluxed for 24 hours at 78°C. The product was purified by recrystallization from ethanol. An orange coloured solid precipitate was collected by filtration, with melting point 308°C (decomp.). Yield 75%.

$^1\text{H NMR}$, 400 MHz, $\text{DMSO}-d_6$: δ = 3.38 ppm (s, 3H) CH_3 ; δ = 6.66 ppm, (d, 3J = 8.4 Hz, 2H) $\text{H}_{1,9}$; δ = 7.61 ppm, (d, 3J = 8.4 Hz, 2H) $\text{H}_{2,8}$; δ = 8.30 ppm, (s, 2H) $\text{CH}=\text{N}$; δ = 7.65 ppm, (s, 2H) $\text{H}_{4,6}$; δ = 7.981 ppm, (d, 3J = 7.6 Hz, 4H) $\text{H}_{2',2''6'6''}$; δ = 7.29 ppm, (d, 3J = 7.6 Hz, 4H) $\text{H}_{3'3'',5'5''}$.

$^{13}\text{C NMR}$, $\text{DMSO}-d_6$: δ (ppm): 35.6 ($-\text{CH}_3$); 115.3 ($\text{C}_{1,9}$), 120.9 ($\text{C}_{2,8}$), 131.2 ($\text{C}_{3,7}$), 159 ($\text{C}=\text{N}$), 125.8 ($\text{C}_{4,6}$), 124.6 ($\text{C}_{4a,5a}$), 147.8, 143.1 ($\text{C}_{9a,10a}$), 130.6 ($\text{C}_{2'2'',6'6''}$), 138.8 ($\text{C}_{1'1''}$), 121.0 ($\text{C}_{3'3'',5'5''}$), 128.5 ($\text{C}_{4'4''}$).

***4,4'*-methylenebis(*N*-(10*H*-phenothiazin-3-yl)methylene)aniline)-4,4'-methylenedianiline 6**

3-formil-10*H*-phenothiazine 0.6g (2.6mmol) and *p,p'*-diamino-diphenyl-methane 0.26g (1.3mmol) in ethyl alcohol was refluxed for 6 hours. The product was filtered and then purified by recrystallization from toluene. A lemon yellow coloured solid precipitate was collected by filtration, with melting point 310°C. Yield 65%. m/z = 616 (M^+ , rel. int. 100%)

$^1\text{H NMR}$, 400 MHz, $\text{DMSO}-d_6$: δ = 3.95 ppm, (s, 2H) $-\text{CH}_2-$; δ = 6.73 ppm, (d, 3J = 8.4 Hz, 2H) H_1 ; δ = 6.93 ppm, (d, 3J = 8.4 Hz, 2H) H_2 ; δ = 8.36 ppm, (s, 2H) $\text{CH}=\text{N}$; δ = 7.43 ppm, (s, 2H) H_4 ; δ = 7.51 ppm, (d, 3J = 8.4 Hz, 2H) H_6 ; δ = 6.79 ppm, (t, 3J = 8.4 Hz, 2H) H_7 ; δ = 7.10 ppm, (t, 3J = 8.4 Hz, 2H) H_8 ; δ = 6.70 ppm, (d, 3J = 8 Hz, 2H), H_9 ; δ = 7.14 ppm, (d, 3J = 8.4 Hz, 4H), $\text{H}_{2'2'',6'6''}$; δ = 7.25 ppm, (d, 3J = 8.4 Hz, 4H) $\text{H}_{3'3'',5'5''}$; δ = 9.01 ppm, (s, 2H) NH .

$^{13}\text{C NMR}$, $\text{DMSO}-d_6$: δ ppm: 114.1 (C_1), 125.2 (C_2), 158.4 ($\text{C}=\text{N}$), 126.1 (C_4), 128.9 (C_6), 122.5 (C_7), 127.7 (C_8), 114.7 (C_9), 144.5 (C_{9a}), 148.3 (C_{10a}), 122.9 (C_{5a}) 123.9 (C_{4a}) 138.7 ($\text{C}_{1',1''}$), 121.0 ($\text{C}_{2'2'',6'6''}$), 130.6 ($\text{C}_{3'3'',5'5''}$), 138.7 ($\text{C}_{4',4''}$), 40.9 (CH_2).

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