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Novel metallophthalocyanines bearing 3-(*p*-chlorophenyl)-5-*p*-tolyl-4*H*-1,2,4-triazole bulky substituents by microwave irradiation

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ABSTRACT

The synthesis of metallophthalocyanines [**6**–**9**; M = Ni(II), Zn(II), Co(II) and Cu(II)] with four 1,2,4-triazole units obtained from 4-{(4-chloro-2-fluorobenzyl)[3-(4-chlorophenyl)-5-(4-methylphenyl)-4*H*-1,2,4-triazol-4-yl]amino}phthalonitrile (**5**) in the presence of dimethylaminoethanol and the corresponding anhydrous metal salts is described. The thermal stabilities of the Pc compounds were determined by thermogravimetric analysis. The new compounds were characterized by a combination of IR, ^{1}H NMR, ^{13}C NMR, UV–Vis, elemental analysis.

1. Introduction

1,2,4-Triazole and its derivatives belong to a class of exceptionally active compounds possessing a wide spectrum of biological properties, including anticonvulsant [1], antimicrobial [2,3], antihypertensive [4], analgesic [5], antiviral [6], antioxidant [7], anti-inflammatory [8], antitumor [9,10], anti-HIV [11], pesticidal [12], insecticidal [13], herbicidal [14] and fungicidal activity [15]. In addition, it was reported that compounds having triazole moieties, such as vorozole, letrozole and anastrazole appeared to be very effective aromatase inhibitors, which in turn prevented breast cancer [16–18]. Apart from their pharmacological significance, 1,2,4-triazole derivatives exhibit interesting chemical properties. The ability of triazoles to form a bridge between metal ions makes such ligands very important for magnetochemical applications [19,20]. Some complexes containing substituted 1,2,4-triazole ligands have potential uses as optical sensors or molecular-based memory devices [21,22].

Phthalocyanines, a family of a aromatic macrocycles depend on delocalized 18-π electron system, are known not only as classical dyes in practical use, but also as modern functional materials in scientific research [23,24].

The importance of phthalocyanines in many fields, including photodynamic reagents for cancer therapy [25], laser dyes, new red-sensitive photocopying applications [26], optical computer read/write discs [27], is increasing rapidly as a result of the synthesis of new compounds [28].

In last years, much effort has been dedicated to the microwave assisted synthesis of metal-free and metallophthalocyanines [29–43]. In this paper, we describe the synthesis and characterization of metallophthalocyanines **6**, **7**, **8** and **9** by microwave irradiation containing 1,2,4-triazole bulky substituents.

2. Experimental

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [44]. The IR spectra were recorded on a Perkin–Elmer 1600 FT-IR Spectrophotometer, using KBr pellets or NaCl disc. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, DMSO, and chemical shifts were reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. The elemental analyses were performed on a Costech ECS 4010 instrument. A Seiko II Exstar 6000 thermal analyzer was used to record DTA curves under nitrogen atmosphere with a heating rate of 20 °C min^{-1} in the temperature range 30–900 °C using platinum crucibles. Melting points were measured on an electrothermal apparatus and are uncorrected. Optical spectra in the UV–Vis region were recorded with a Unicam UV2-100 spectrophotometer, using 1 cm pathlength cuvettes at room temperature.

2.1. Ethyl p-methylbenzoate p-chlorobenzoylhydrazone (*1*)

A solution of *p*-chlorobenzhydrazide (0.01 mol) in 25 mL of absolute ethanol was added to a solution of ethyl imido-*p*-meth-

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ylbenzoate hydrochloride (0.01 mol) in 25 mL of absolute ethanol. The mixture was stirred for 6 h at 0–5 °C and subsequently for 2 h at room temperature. The reaction mixture was poured into a beaker containing 40 mL of cold water and 10 g of ice. The precipitate formed was washed with 50 mL of ice-water and then dried. The product was recrystallized from benzene–petroleum ether (1:2) to give pure compound **1**. Yield 78%, m.p. 105–106 °C. IR (KBr tablet), ν_{max}/cm^{-1}: 3178 (N–H), 3067 (Ar–H), 2976–2925 (Aliph. C–H), 1646 (C=O), 1564, 1456, 1398, 1378, 1299, 1089, 1070, 1014, 847, 814, 793. ^{1}H NMR (DMSO-d_6) δ = 10.27 (s, 1H, NH), Ar–H: [7.83 (2H, J = 8.40 Hz), 7.66 2H, J = 8.00 Hz), 7.45 (2H, J = 8.40 Hz), 7.21 (2H, J = 8.00 Hz)], 4.29 (q, 2H, J = 3.60 Hz, OCH_2CH_3), 2.28 (s, 3H, CH_3), 1.27 (t, 3H, J = 3.60 Hz, OCH_2CH_3). ^{13}C NMR (DMSO-d_6) δ = 165.92 (C=O), 162.06 (C=N), Ar–C: [140.87, 136.47, 130.38, 129.97 (2C), 129.68 (2C), 129.05 (2C), 128.50 (2C), 128.33], 67.40 (OCH_2CH_3), 21.64 (CH_3), 14.87 (OCH_2CH_3).

2.2. 4-Amino-3-(p-chlorophenyl)-5-p-tolyl-4H-1,2,4-triazole (**2**)

Compound **1** (0.005 mol) was added to a solution of hydrazine hydrate (0.01 mol) in 50 mL of 1-propanol and the mixture was refluxed for 24 h. On cooling, a precipitate was formed. This product was filtered and, after drying, was washed with 20 mL of benzene. The remaining solid was recrystallized from 1-propanol to afford pure compound **2**. Yield 85%, m.p. 314–315 °C. IR (KBr tablet), ν_{max}/cm^{-1}: 3360–3206 (NH_2), 3035, 2921, 1619 (C=N), 1474, 1269, 1093, 1015, 968, 911, 823, 727. ^{1}H NMR (DMSO-d_6) δ = Ar–H: [8.02 (d, 2H, J = 7.4 Hz), 7.92 (d, 2H, J = 6.8 Hz), 7.52 (d, 2H, J = 6.8 Hz), 7.34 (d, 2H, J = 7.4 Hz)], 6.26 (s, 2H, NH_2), 2.38 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6) δ = 154.93 (triazole C_5), 154.81 (triazole C_3), Ar–C: [139.91, 130.22, 129.73 (2C), 129.16 (2C), 128.98 (2C), 128.88 (2C), 127.99, 125.09], 21.70 (CH_3).

2.3. 3-(p-chlorophenyl)-5-p-tolyl-4-(2-fluoro-4-chlorobenzylidenamino)-4H-1,2,4-triazole (**3**)

4-Chloro-2-fluorobenzaldehyde (0.005 mol) was added to a solution of compound **2** (0.005 mol) in 20 mL of glacial acetic acid and the mixture was refluxed for 4 h. After cooling, the mixture was poured into a beaker containing 100 mL of ice-water. The precipitate formed was filtered. After drying *in vacuo*, the solid was recrystallized from ethanol–water (1:2) to afford pure compound **3**. Yield 87%, m.p. 175–176 °C; Anal. Calc. for $C_{22}H_{15}Cl_2FN_4$: C: 62.13, H: 3.55, N: 13.17. Found: C: 62.12, H: 3.57, N: 13.19%. IR (KBr tablet), ν_{max}/cm^{-1}: 1608, 1565 (C=N), 909, 823, 724 (arom. ring) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 8.37 (s, 1H, N=CH), Ar–H: [8.07–7.99 (m, 1H), 7.86 (d, 2H, J = 8.4 Hz), 7.69 (d, 2H, J = 8.0 Hz), 7.44 (d, 2H, J = 8.4 Hz), 7.32–7.24 (m, 3H), 7.17–7.11 (m, 4H)], 2.39 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ = 160.43 (C=N), 154.42 (triazole C-5), 151.57 (triazole C-3), Ar–C: [164.23, 140.40, 136.14, 134.75, 129.83 (2C), 129.71 (2C), 129.60, 129.11 (2C), 128.53 (2C), 125.91, 124.89, 123.13, 117.53, 117.04, 21.46 (CH_3).

2.4. 3-(p-chlorophenyl)-5-p-tolyl-4-(2-fluoro-4-chlorobenzylamino)-4H-1,2,4-triazole (**4**)

Compound **3** (0.005 mol) was dissolved in 50 mL of dried methanol, and $NaBH_4$ (0.005 mol) was added in small portions to this solution. The mixture was refluxed for 30 min and then allowed to cool. After evaporation at 25–30 °C under reduced pressure, the solid residue was washed with cold water. After drying *in vacuo*, the solid product was recrystallized from an ethanol to afford pure compound **4**. Yield 95%, m.p. 202–203 °C; Anal. Calc. for $C_{22}H_{17}Cl_2FN_4$: C: 61.84, H: 4.01, N: 13.11. Found: C: 61.87, H: 4.02, N: 13.16%. IR (KBr tablet), ν_{max}/cm^{-1}: 3250 (NH), 1610, 1581 (C=N), 895, 819, 731 (arom. ring) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = Ar–H: [7.83 (d, 2H, J = 8.8 Hz), 7.64 (d, 2H, J = 8.4 Hz), 7.42 (d, 2H, J = 8.8 Hz), 7.31 (d, 2H, J = 8.4 Hz), 6.87–6.82 (m, 1H), 6.73–6.67 (m, 1H), 6.61-6.53 (m, 1H)], 5.68 (t, 1H, J = 4.4 Hz, NH), 3.77 (d, 2H, J = 4.4 Hz, CH_2), 2.45 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ = 164.57 (C=N), 154.05 (triazole C-5), 152.51 (triazole C-3), Ar–C: [163.38, 140.65, 136.09, 135.49, 131.83, 129.73, 129.46, 129.24 (2C), 128.78 (2C), 127.73 (2C), 124.42, 123.34, 120.21, 116.36], 49.47 (CH_2), 21.50 (CH_3).

2.5. 4-{(4-chloro-2-fluorobenzyl)[3-(4-chlorophenyl)-5-(4-methylphenyl)-4H-1,2,4-triazol-4-yl]amino}phthalonitrile (**5**)

N-(4-chloro-2-fluorobenzyl)-3-(4-chlorophenyl)-5-(4-methylphenyl)-4*H*-1,2,4-triazol-4-amine **4** (1.5 g, 3.51 mmol) and 4-nitrophthalonitrile (607 mg, 3.51 mmol) were dissolved in dry DMF (10 mL) under N_2 atmosphere. After stirring for 10 min at 50 °C, dry fine-powdered potassium carbonate (968 mg, 7.02 mmol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under N_2 at 50 °C for 3 days. Then the mixture was poured into 150 mL ice-water, and precipitate was filtered off, washed with water, diethyl ether and dried *in vacuo*. The residue was crystallized from ethanol. Yield: 1.03 g (53%), m.p. 162–163 °C. Anal. Calc. for $C_{30}H_{19}N_6Cl_2F$: C, 65.11; H, 3.46; N, 15.19. Found: C, 65.10; H, 3.86; N, 15.14%. IR (KBr tablet), ν_{max}/cm^{-1}: 3071 (Ar–H), 2921–2862 (Aliph. C–H), 2228 (C≡N), 1600, 1581, 1531, 1488, 1411, 1345, 1269, 1185, 1093, 1015, 896, 821, 731, 592, 521. ^{1}H NMR. (DMSO-d_6), (δ:ppm): Ar–H: [8.03 (d, 2H), 7.91 (m, 2H), 7.81 (m, 2H), 7.73 (s, 1H), 7.55 (d, 2H, J = 5.0 Hz), 7.27 (d, 2H, J = 4.7 Hz), 7.04–6.99 (m, 1H), 6.94-6.87 (m, 1H), 6.78–6.70 (m, 1H)], 3.73 (s, 2H, CH_2), 2.48 (s, 3H, CH_3). ^{13}C NMR. (DMSO-d_6), (δ:ppm): 163.22, 161.52, 158.34, 150.08, 139.74, 135.28, 134.50, 133.59, 132.46, 129.58, 129.22, 128.41, 127.68, 127.38, 125.98, 125.61, 124.19, 123.87, 121.74, 121.44, 117.44, 116.72, 115.77, 115.26, 105.80, 48.24, 21.42.

2.6. General procedures for phthalocyanine derivatives (**6**–**9**)

A mixture of 4-{(4-chloro-2-fluorobenzyl)[3-(4-chlorophenyl)-5-(4-methyl phenyl)-4*H*-1,2,4-triazol-4-yl]amino}phthalonitrile **5** (230 mg, 0.41 mmol), anhydrous metal salt [$NiCl_2$ (14 mg), $Zn(CH_3COO)_2$ (19 mg), $CoCl_2$ (13 mg), $CuCl_2$ (14 mg)] and 2-(dimethylamino)ethanol (3 mL) was irradiated in a microwave oven at 175 °C, 350 W for 8 min. After cooling to room temperature the reaction mixture was refluxed with ethanol to precipitate the product which was filtered off. The green solid product was washed with hot ethanol, water, diethyl ether and dried *in vacuo* over P_2O_5.

2.7. Phthalocyaninato nickel(II) (**6**)

Yield: 142 mg (60%). Anal. Calc. for $C_{120}H_{76}N_{24}Cl_8F_4Ni$: C, 63.43; H, 3.37; N, 14.79. Found: C, 63.40; H, 3.31; N, 14.76%. IR (KBr tablet) ν_{max}/cm^{-1}: 3060 (Ar–H), 2923–2857 (Aliph. C–H), 1608, 1484, 1472, 1410, 1218, 1093, 1056, 894, 820. ^{1}H NMR. (DMSO), (δ:ppm): 7.83–7.33 (m, 56H, Ar–H), 3.79 (s, 8H, CH_2–N), 2.25 (s, 12H, CH_3).

2.8. Phthalocyaninato zinc(II) (**7**)

Yield: 125 mg (53%). Anal. Calc. for $C_{120}H_{76}N_{24}Cl_8F_4Zn$: C, 63.24; H, 3.36; N, 14.75. Found: C, 63.20; H, 3.30; N, 14.59%. IR (KBr tablet) ν_{max}/cm^{-1}: 3060 (Ar–H), 2917–2846 (Aliph. C–H), 1608, 1580, 1486, 1448, 1407, 1341, 1215, 1182, 1091, 1012, 894, 820. ^{1}H NMR. (DMSO), (δ:ppm): 7.90–7.41 (m, 56H, Ar–H), 3.85 (s, 8H, CH_2–N), 2.23 (s, 12H, CH_3).

*2.9. Phthalocyaninato cobalt(II) (**8**)*

Yield: 134 mg (57%). Anal. Calc. for $C_{120}H_{76}N_{24}Cl_8F_4Co$: C, 63.42; H, 3.37; N, 14.79. Found: C, 63.37; H, 3.28; N, 14.77%. IR (KBr tablet) ν_{max}/cm^{-1}: 3065 (Ar–H), 2923–2851 (Aliph. C–H), 1607, 1580, 1484, 1410, 1382, 1218, 1179, 1092, 894, 820.

*2.10. Phthalocyaninato copper(II) (**9**)*

Yield: 149 mg (63%). Anal. Calc. for $C_{120}H_{76}N_{24}Cl_8F_4Cu$: C, 63.29; H, 3.36; N, 14.76. Found: C, 63.33; H, 3.38; N, 14.71%. IR (KBr tablet) ν_{max}/cm^{-1}: 3027 (Ar–H), 2923–2851 (Aliph. C–H), 1603, 1488, 1454, 1410, 1341, 1262, 1220, 1179, 1091, 1009, 896, 821.

3. Results and discussion

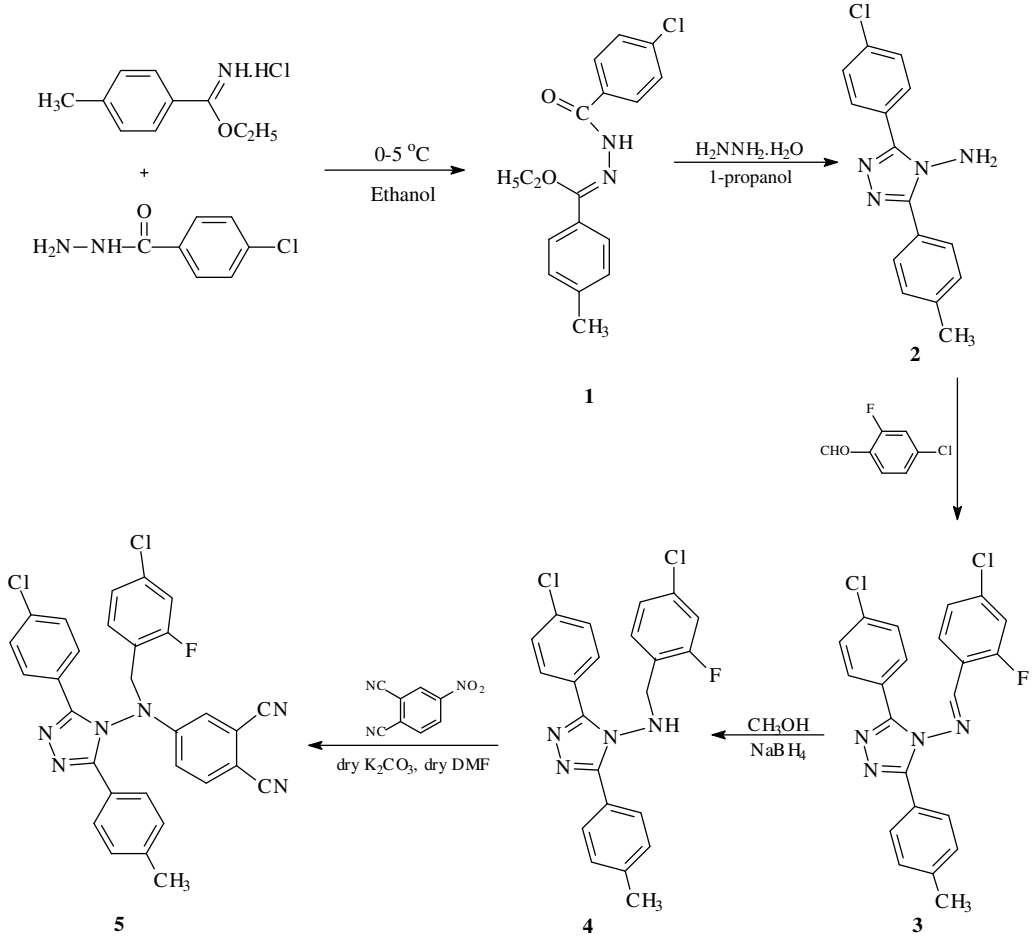
In the current study, ethyl *p*-methylbenzoate *p*-chlorobenzoylhydrazone **1** was synthesized from the reaction of ethyl imido-*p*-methylbenzoate hydrochloride with *p*-chlorobenzhydrazide. 4-amino-3-(*p*-chlorophenyl)-5-*p*-tolyl-4*H*-1,2,4-triazole **2** was obtained from the reaction of compound **1** with hydrazine hydrate in 1-propanol. Compound **2** was treated with 4-chloro-2-fluorobenzaldehyde in acetic acid to give 3-(*p*-chlorophenyl)-5-*p*-tolyl-4-(2-fluoro-4-chlorobenzylidenamino)-4*H*-1,2,4-triazole **3**. Then compounds **3** were converted to 3-(*p*-chlorophenyl)-5-*p*-tolyl-4-(2-fluoro-4-chlorobenzylamino)-4*H*-1,2,4-triazole **4** by treatment with $NaBH_4$ in methanol. Next step in the synthetic procedure was to obtain 4-{(4-chloro-2-fluorobenzyl)[3-(4-chlorophenyl)-5-(4-methylphenyl)-4*H*-1,2,4-triazol-4-yl]amino}-phthalonitrile **5**. The phthalonitrile derivative **5** was obtained through displacement reaction of 4-nitrophthalonitrile with compound **4**. Metallophthalocyanines **6**–**9** were prepared from the corresponding phthalonitrile 5 and corresponding metal salts (Ni, Zn, Co, Cu) in dimethylaminoethanol for 8 min 175 °C, 350 W by microwave (Scheme 1). The structures of novel compounds were characterized by a combination of ^1H NMR, ^{13}C NMR, IR, UV–Vis, elemental analysis Scheme 2.

3.1. IR spectra

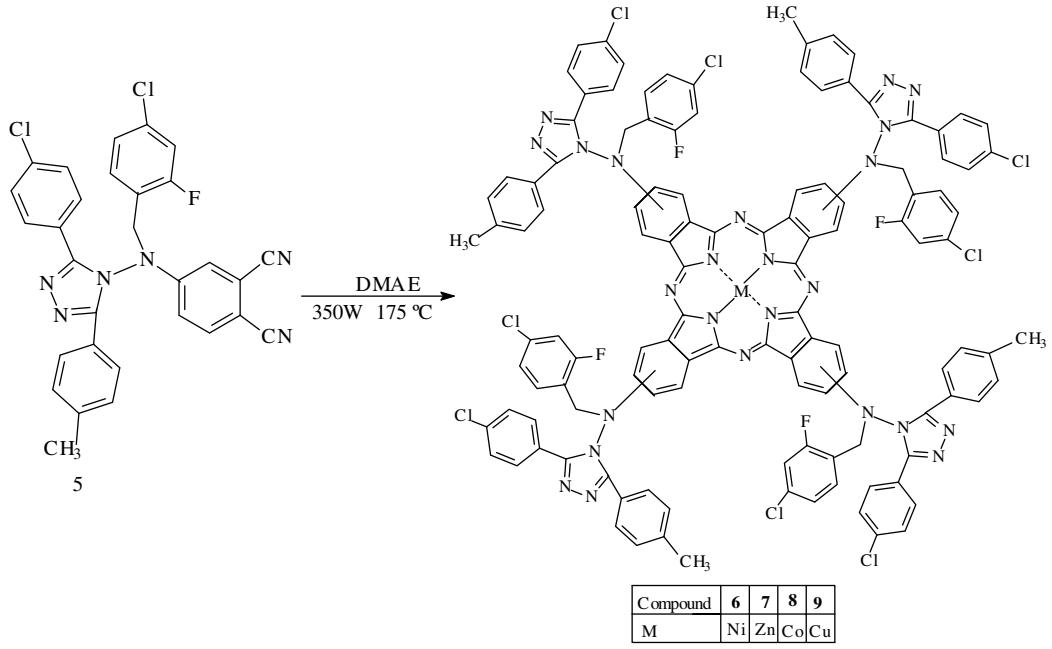
The IR spectra of compound **1** showed absorption bands in the 3178, 1649 and 1619 cm^{-1} regions resulting from the NH, C=O and C=N functions, respectively. Compound **2** showed two peaks in the regions 3343–3206 cm^{-1} due to asymmetric and symmetric vibration of the primary amino group. Compound **3** showed characteristic C=N stretching bands between 1565 and 1608 cm^{-1}. Characteristic NH stretching bands of **4** was observed at 3250 cm^{-1}. The formation of dinitrile derivative **5** was clearly indicated by the appearance in its FT-IR spectrum of the C≡N band at 2228 cm^{-1}. After conversion of dinitrile derivative **5** to metallophthalocyanine **6**–**9**, the sharp C≡N vibration around 2228 cm^{-1} disappeared.

3.2. NMR spectra

In the ^1H NMR spectra of compound **1** characteristic OCH_2CH_3 signals appeared at δ 4.29 ppm (q, 2H, CH_2) and δ 1.27 ppm (t, 3H, CH_3). Characteristic amino proton (NH_2) of compound **2** was



Scheme 1. The synthesis of dinitrile compound.



Scheme 2. The synthesis of metallophthalocyanines.

detected at δ 6.26 ppm. The ^{1}H NMR characteristic signals of Schiff base (**3**) were observed at δ 8.37 ppm (s, 1H, N=CH). The ^{1}H NMR signals for the $-CH_2-$ group of compound **4** were observed as a doubled at δ 3.77 (J = 4.4 Hz) ppm and the proton signals of –NH– group was recorded as a triplet at δ 5.68 (J = 4.4 Hz) ppm. In the ^{1}H NMR spectrum of **5**, NH group of compound **4** disappeared as expected. In the ^{13}C NMR spectra of compound **1** characteristic C=O signal appeared δ 165.92 ppm. The Triazole C-3 and C-5 signals of compound **2** were recorded at δ 154.81 ppm and δ 154.93 ppm, respectively. The ^{13}C characteristic N=CH carbon signal of compound **3** was recorded at δ 160.43 ppm. Characteristic $NH-CH_2$ carbon signal of compound **4** was recorded at δ 49.47 ppm. In the ^{13}C NMR spectrum of **5** indicated the presence of nitrile carbon atoms in **5** at δ = 115.26 and 115.77 ppm.

3.3. UV-Vis spectra

The electronic absorption spectrum of the metallophthalocyanines **6**,**7** and **8**,**9** in pyridine at room temperature is shown in Figs. 1 and 2, respectively. UV–Vis spectra of phthalocyanine core is dominated by two intense bands, the Q band around 600–710 nm and the B band in the near UV region at about 300–400 nm, both correlated $\pi-\pi^*$ transitions. The UV–Vis absorption spectra of metallophthalocyanines **6**–**9** in pyridine show intense Q absorption at λ_{max} = 701, 709, 703 and 704 nm, with a weaker

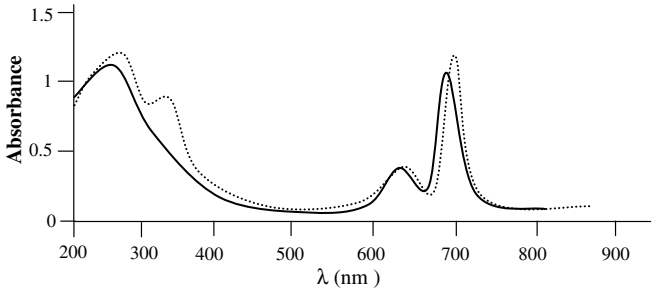


Fig. 1. UV–Vis spectra of compounds **6** (–), **7** (. . .) in pyridine.

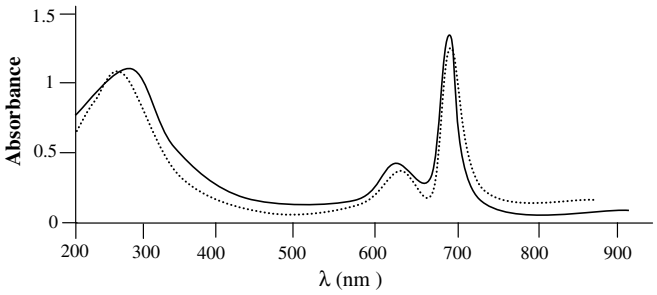


Fig. 2. UV–Vis spectra of compounds **8** (–), **9** (. . .) in pyridine.

absorptions at 641, 643, 633 and 637 nm, respectively. The single Q bands in metallo derivatives **6**–**9** are characteristic. This result is typical of metal complexes of substituted and unsubstituted metallophthalocyanines with D_{4h} symmetry [45]. B band absorptions of compounds **6**–**9** were observed at λ_{max} = 271, (280, 357), 300, 293 nm as expected, respectively.

3.4. TG/DTA

The thermal behaviour of the metallophthalocyanines were investigated by TG/DTA. Although the thermal stabilities of phthalocyanines is well known, the phthalocyanines compounds are not stable above 338 °C. The initial and main decomposition temperatures are given in Tables 1 and 2. The initial decomposition temperature decreased in the order: **8** > **9** > **6** > **7**.

Table 1
UV–Vis data for the phthalocyanines

Compound	Solvent	λ_{max}/nm: [10^{-5} ε (dm^3 mol^{-1} cm^{-1})]
6	Pyridine	271 (5.04), 641 (4.50), 701 (5.00)
7	Pyridine	280 (5.08), 357 (4.92), 643 (4.50), 709 (5.04)
8	Pyridine	300 (5.03), 633 (4.56), 703 (5.12)
9	Pyridine	293 (5.01), 637 (4.54), 704 (5.08)

Table 2
Thermal properties of the phthalocyanines

Compound	M	Initial decom. temp. (°C)	Main decom. temp. (°C)
6	Ni	343	398
7	Zn	338	399
8	Co	371	422
9	Cu	359	412

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