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Microwave-Assisted Synthesis of Some Metal-Free Phthalocyanine Derivatives and a Comparison with Conventional Methods of their Synthesis

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Synthesis of metal-free 2,9(10),16(17),23(24)-tetra(3,5-dimethylphenoxy) phthalocyanine, 2,9(10),16(17), 23(24)-tetra(4-*tert*-butylphenoxy) phthalocyanine, and 2,9(10),16(17),23(24)-tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl) phthalocyanine was carried out via microwave irradiation. Furthermore, pentanol and lithium were used for the first time in the synthesis of metal-free phthalocyanine under microwave irradiation as a solvent and a base-catalyst, respectively. The microwave irradiation experiments were performed in a MARS5 with a CEM XP-1500 vessel. In addition, these compounds were obtained with conventional heating procedures to compare them with those obtained with microwave irradiation. The compounds were characterized by elemental and spectroscopic analysis, including UV-Vis, ^{1}H NMR, FT-IR, and MALDI-TOF mass data. In particular, both methods were compared in terms of reaction parameters and product yields. In addition, we first performed the synthesis of phthalonitriles as an initial material at room temperature, which is a slight modification of that reported in the literature.

These Pc-compounds had high thermal stability, which was determined at 520 °C (midpoint), 549 °C, and 400 °C, respectively, as a maximum weight loss temperature.

Consequently, the microwave irradiation method provided nearly the same or higher product yields in a very short period of time. These results suggest that the microwave irradiation method was more useful than the conventional method due to shorter reaction time and energy savings.

Key Words: Synthesis; metal-free phthalocyanines; microwave irradiation; conventional heating; lithium, pentanol.

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Introduction

Phthalocyanines (Pcs) are traditionally used as dyes and pigments.[1] Their characteristic blue-green color and robustness account for their traditional use as industrial pigments.[2] Their use has recently extended to many high technological processes. They can be used in many applications with appropriate substitution in the peripheral position of the macrocycle, such as in optical recording materials, optical limiters, field-effect transistors, Langmuir-Blodgett films,[3] thin films (or solar cells),[4] gas sensors,[5] and liquid crystals.[6] Furthermore, they are used as catalysts for photo or oxidative degradation of pollutants,[7] and as photosensitizers for photodynamic therapy.[8] The synthetic methodologies for this class of compounds are relatively well established.

Metal-free analogues, which can serve as precursors for various metallophthalocyanines, are usually prepared via base-promoted cyclization of phthalonitriles. Some typical procedures involve treatment with 1,8-diazabicylo[5,4,0]undec-7-ene (DBU) or lithium metal in alcohol (followed by acidic work-up).[2]

In the last decade increased interest has been focused on the application of microwave irradiation in organic synthesis.[9,10] Numerous reactions can be performed under microwave-assisted conditions; significant rate enhancements, improved yield and selectivity, and a reduction in thermal by-products have been described.[9,11] It is probable that the increased yields and drastically reduced reaction times are caused by an elevation in the boiling point of the solvent due to a non-nucleated boiling process.[12]

The microwave-assisted synthesis of some phthalocyanine derivatives has recently been investigated. The microwave heating synthesis of (phthalocyaninato)-bis(chloro)silicon(IV) prepared from diiminoisoindoline and silicon tetrachloride in quinoline has been reported by Davies et al.[12]

The synthesis of soluble and fluorescent phthalocyanine-perylene tetracaboxylic complexes (Pc-Pe complexes) under microwave irradiation has been reported.[10] A soluble phthalocyanine-porphyric complex has been rapidly synthesized from a lutetium porphyrin and a metal-free phthalocyanine under microwave irradiation.[13]

Burczyk et al. applied microwave irradiation to the synthesis of phthalocyanines under solvent-free conditions in order to determine how such a non-classical method of chemical activation might influence yield, selectivity, and reaction time in comparison to conventional thermal treatment under strictly similar sets of conditions.[11]

Shaabani et al. reported the possibility of synthesizing metal-free phthalocyanine and metallophthalocyanines from phthalonitrile, phthalimide, and phthalic anhydride via treatment with hexamethylsilazane and microwave irradiation.[14]

In another study Biyiklioğlu et al. investigated the synthesis of metal-free and metallophthalocyanines bearing tetraaza macrocyclic moieties under microwave irradiation.[15]

This synthetic work demonstrates that it is possible to obtain metal-free 2,9(10),16(17),23(24)-tetra(3,5-dimethylphenoxy) phthalocyanine(**8**), 2,9(10),16(17),23(24)-tetra(4-*tert*-butylphenoxy) phthalocyanine (**9**), and 2,9(10),16(17),23(24)-tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl)phthalocyanine (**10**) with microwave irradiation, which is a new method for these derivatives. Additionally, these compounds have also been obtained by conventional heating procedures in order to compare them to each other.[16] We preferred to use the same parameters and conditions for both procedures, including solvents, amount of precursors, and temperature. We compared the results and product yields of 2 different procedures.

Experimental

4-Nitrophthalonitrile and 4-*tert*-butylphenol were purchased from Fluka, 3,5-dimethylphenol and 2,6-di-*tert*-butylphenol were purchased from Aldrich, and n-pentanol and lithium (Li) were purchased from Merck. Silica gel (Merck) was used in the separation and purification of the compounds by column chromatography, and by preparative chromatography.

^{1}H NMR spectra were recorded on a Varian AS 400 Mercury instrument, IR spectra were measured with a Perkin-Elmer Fourier transform infrared spectrometer using KBr pellets. Elemental analyses were performed at the TÜBİTAK Ankara Test and Analysis Laboratory. MALDI-TOF MS spectra were analyzed on an Applied Biosytems Voyager instrument using 1,8,9-anthracene triol as the matrix. The microwave experiments were performed in a CEM MARS5 microwave system (total power: 1200 W) equipped with an XP-1500 vessel. UV-Vis spectra of the phthalocyanines compounds were measured with a Specord 600 UV-Vis spectrophotometer. UV-Vis spectra were measured in chloroform. Thermogravimetric analyses (TGA) were performed using a Perkin Elmer Pyris 6 TGA in a nitrogen atmosphere, with a heating rate of 20 °C/min. Routine melting point determination was carried out with an electrothermal melting point apparatus.

Preparation of Derivatives of Phthalonitrile

In the present study, first phthalonitriles were synthesized as an initial material at room temperature via a procedure that was modified slightly from earlier reports.

4-(3,5-dimethylphenoxy)phthalonitrile (5)

In an argon atmosphere, 1.59 g (11.5 mmol) of anhydrous potassium carbonate (K_2CO_3) was added in 0.53-g portions at 1-h intervals to a solution of 1.49 g (11.5 mmol) of 3,5-dimethylphenol and 1 g (5.75 mmol) of 4-nitrophthalonitrile in 10 mL of dry N,N-dimethylformamide (DMF). The mixture was stirred for 72 h at room temperature in the same atmosphere. After 72 h the undissolved salt was filtered, 200 mL of cold water was added, and then the mixture was stirred rapidly. The resulting precipitate was filtered by vacuum and washed with water. The crude product was recrystallized twice from ethanol.

White crystals. Yield: 52%; mp: 119-121 °C. **IR (KBr)** ν**, cm**$^{-1}$: 3077, 2921, 2229, 1617, 1600, 1584, 1494, 1313, 1248, 1198, 1166, 1131, 1086, 1022, 999, 960, 850, and 837; ^{1}**H NMR** ($CDCl_3$): δ 6.6-7.8(Ar-H, 6H), 2.5 (s, 6H), and $C_{16}H_{12}N_2O$; $\mathbf{M}_W$: 248.28 g/mol.

4-(4-*tert*-butylphenoxy)phthalonitrile (6)

In an argon atmosphere, 1.59 g (11.48 mmol) of anhydrous K_2CO_3 was added in 0.53-g portions at 1-h intervals to a solution of 1.72 g (11.48 mmol) of 4-*tert*-butylphenol and 1 g (5.74 mmol) of 4-nitrophthalonitrile in 10 mL of dry N,N-dimethylformamide (DMF). The mixture was stirred for 48 h at room temperature under argon. After 48 h the undissolved salt was filtered, 200 mL of cold water was added, and then the mixture was stirred rapidly. The resulting precipitate was filtered by vacuum and washed with water. The crude product was recrystallized from ethanol.

White crystals. Yield: 47%; mp: 114-116 °C. **IR (KBr)** ν**, cm**$^{-1}$: 3080, 3059, 2959, 2229, 1587, 1500, 1480, 1313, 1279, 241, 109, 1179, 1109, 1088, 1019, 949, and 840; ^{1}**H NMR** ($CDCl_3$): δ 6.97-7.71 (Ar-H, 7H), 1.35 (s, 9H), and $C_{18}H_{16}N_2O$; $\mathbf{M}_W$: 276.34 g/mol.

4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)phthalonitrile (7)

In an argon atmosphere, 1.7 g (12.3 mmol) of anhydrous K_2CO_3 was added in 0.56-g portions at 1 h intervals to a solution of 2.86 g (13.8 mmol) of 2,6-di-*tert*-butylphenol and 1 g (5.75 mmol) of 4-nitrophthalonitrile in 10 mL of dry *N*, *N*-dimethylformamide (DMF). The mixture was stirred for 48 h at room temperature under argon. After 48 h the undissolved salt was filtered, 200 mL of cold water was added, and then the mixture was stirred rapidly. The resulting precipitate was filtered by vacuum and washed with water. The crude product was recrystallized twice from ethanol.

Light yellow prismatic crystals. Yield: 51%; mp: 221-222 °C. **IR (KBr)** ν**, cm**$^{-1}$: 3623, 3072, 2952, 2229, 1594, 1431, 1365, 1314, 1234, 1150, 1119, 889, and 849; ^{1}**H NMR** ($CDCl_3$): δ 7.8-7.93 (Ar, 3H), 7.37 (Ar, 2H), 5.51 (s, 1H), 1.5 (s, 18H), and $C_{22}H_{24}N_2O$; $\mathbf{M}_W$: 332.44 g/mol

Preparation of Phthalocyanine Derivatives

Microwave Method (a)

2,9(10),16(17),23(24)-Tetra(3,5-dimethylphenoxy)Phthalocyanine (8a)

3,5-Dimethyl phenoxy phthalonitrile (200 mg, 0.805 mmol) and 40 mg of Li were ground together in a microwave vessel, and n-pentanol (4 mL) was added. The reaction mixture was irradiated in a microwave reaction oven at 440 W for 10 min. After 10 min the reaction mixture was cooled and acetic acid was added (0.75 mL). The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, chloroform/methanol: 4.9/0.1: eluent). The product was washed several times with hot methanol.

Yield: 21.0%; $\mathbf{M}_W$: 995.15 g/mol; mp: > 350 °C. **IR (KBr)** ν**, cm**$^{-1}$: 3417, 3290, 3036, 2946, 2857, 1612, 1592, 1466, 1425, 1295, 1251, 1225, 1208, 1135, 1092, 1010, 953, 917, and 829; **UV-Vis** ($CHCl_3$)λ: 348 nm, 609 nm, 644 nm, 668 nm, and 704 nm; **MALDI-TOF MS**: m/z = 993.87.

2,9(10),16(17),23(24)-Tetra(4-*tert*-butylphenoxy)Phthalocyanine (9a)

4-(4-*Tert*-butylphenoxy) phthalonitrile (200 mg, 0.724 mmol) and 40 mg Li were ground together in a microwave vessel, and n-pentanol (4 mL) was added. The reaction mixture was irradiated in a microwave reaction oven at 440 W for 10 min. After 10 min the reaction mixture was cooled and acetic acid was added (0.75 mL). The solvent was removed under reduced pressure and then the residue was purified by column chromatography (silica gel, chloroform/methanol: 4.9/0.1: eluent). The product was washed several times with hot methanol.

Yield: 16.0%; $\mathbf{M}_W$: 1107.36g/mol; mp: > 350 °C. **IR (KBr)** ν**, cm**$^{-1}$: 3422, 3291, 3037, 2959, 2866, 1602, 1307, 1475, 1423, 1394, 1321, 1234, 1173, 1108, 1092, 1011, 929, and 827; **UV-Vis** ($CHCl_3$)λ: 347 nm, 610 nm, 642 nm, 669 nm, and 704 nm; **MALDI-TOF MS**: m/z = 1106.50.

2,9(10),16(17),23(24)-Tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl)Phthalocyanine (10a)

4-(3,5-di-*Tert*-butyl-4-hydroxyphenyl)phthalonitrile (200 mg, 0.601 mmol) and 33 mg of Li were ground together in a microwave vessel, and n-pentanol (4 mL) was added. The reaction mixture was irradiated in a microwave reaction oven at 440 W for 10 min. After 10 min the reaction mixture was cooled and acetic acid was added (0.75 mL). The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, chloroform/methanol: 4.9/0.1: eluent, then with chloroform/toluen/hekzan: 2/2/1: eluent) and then preparative chromatography (with methanol as eluent).

Yield: 6.5%; $\mathbf{M}_W$: 1331.79 g/mol; mp: $>$ 350 °C. **IR (KBr)** ν**, cm**$^{-1}$: 3630, 3428, 3288, 2955, 2918, 1615, 1430, 1310, 1232, 1156, 1105, 1009, 881, and 829; **UV-Vis** ($CHCl_3$)λ: 349 nm, 627 nm, 656 nm, 686 nm, and 718 nm; **MALDI-TOF MS**: m/z = 1329.91.

Conventional Method (b)

Phthalocyanines (8b, 9b, and 10b) were synthesized according to a previously reported procedure.[16]

2,9(10),16(17),23(24)-Tetra(3,5-dimethylphenoxy)Phthalocyanine (8b) (representative procedure)

4-(3,5-Dimethylphenoxy)phthalonitrile (200 mg, 0.805 mmol) was dissolved in dry n-pentanol (4 mL). The solution was heated to reflux under an argon atmosphere and Li (40 mg) was added. After 24 h the reaction mixture was cooled and acetic acid was added (0.75 mL). The solvent was removed under pressure and the residue was purified, as mentioned above.

Yield: 14.0%; $\mathbf{M}_W$: 995.15 g/mol; mp: $>$ 350 °C. **IR (KBr)** ν**, cm**$^{-1}$: 3411, 3290, 3014, 2916, 2857, 1612, 1592, 1500, 1467, 1423, 1296, 1251, 1226, 1209, 1135, 1092, 1010, 953, and 918; **UV-Vis** ($CHCl_3$)λ: 348 nm, 609 nm, 644 nm, 668 nm, and 704 nm.

2,9(10),16(17),23(24)-Tetra(4-tertbutylphenoxy)Phthalocyanine (9b)

Yield: 18.4%; $\mathbf{M}_W$: 1107.36g/mol; mp: $>$ 350 °C. **IR (KBr)** ν**, cm**$^{-1}$: 3431, 3291, 3037, 2959, 2903, 2866, 1602, 1508, 1475, 1425, 1394, 1321, 1235, 1173, 1108, 1092, 1011, 928, and 827; **UV-Vis** ($CHCl_3$)λ: 347 nm, 610 nm, 642 nm, 669 nm, and 704 nm.

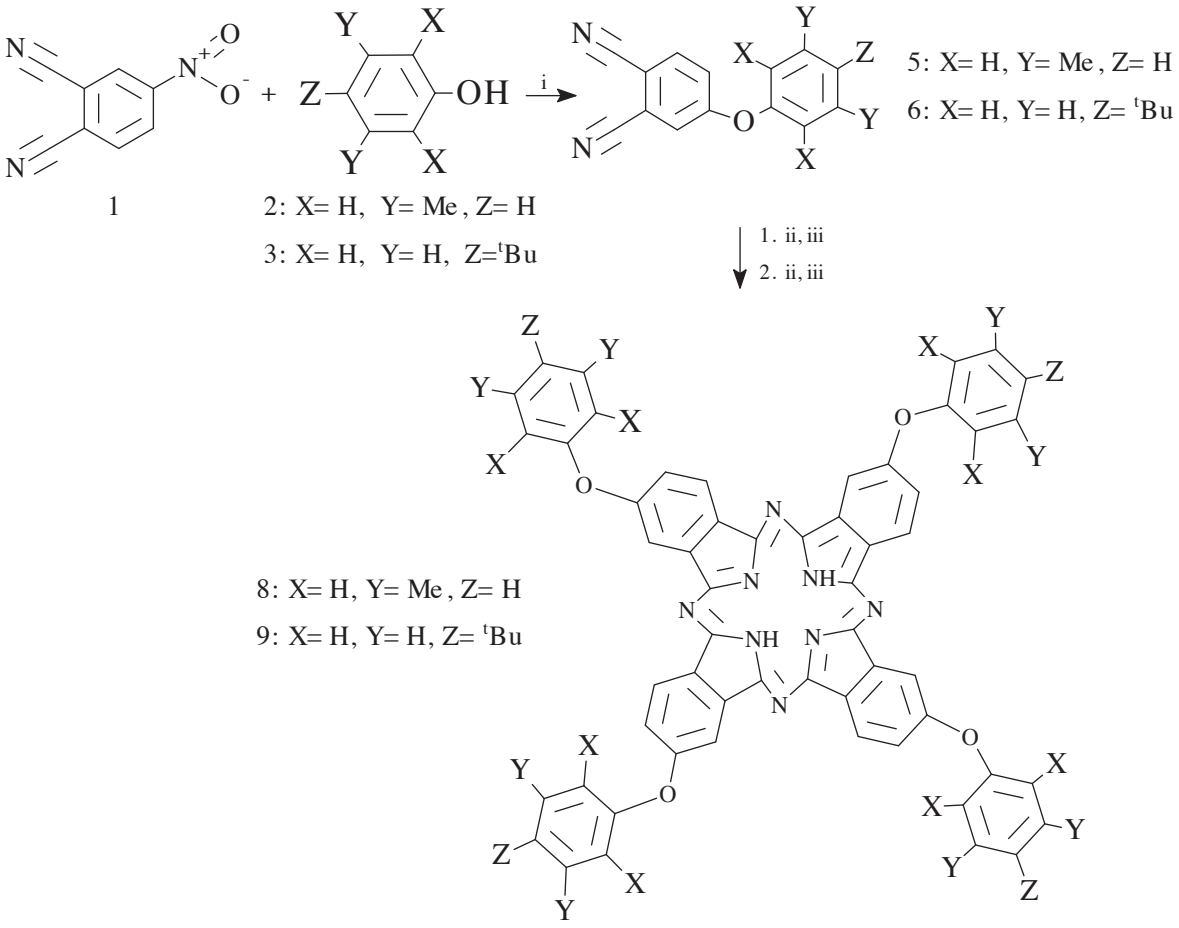
2,9(10),16(17),23(24)-Tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl)Phthalocyanine (10b)

Yield: 6.7%; $\mathbf{M}_W$: 1331.79 g/mol; mp: $>$ 350 °C. **IR (KBr)** ν**, cm**$^{-1}$: 3631, 3417, 3293, 3058, 2956, 2862, 1609, 1431, 1310, 1232, 1157, 1105, 1010, 925, 882, and 830; **UV-Vis** ($CHCl_3$)λ: 349 nm, 627 nm, 656 nm, 686 nm, and 718 nm.

Results and Discussion

In the present study, as an initial material we first performed the synthesis of phthalonitriles at room temperature. This procedure was a slight modification of earlier reports. The synthesis of the tetra-substituted metal-free phthalocyanines via conventional and microwave methods are depicted in Schemes 1 and 2. The

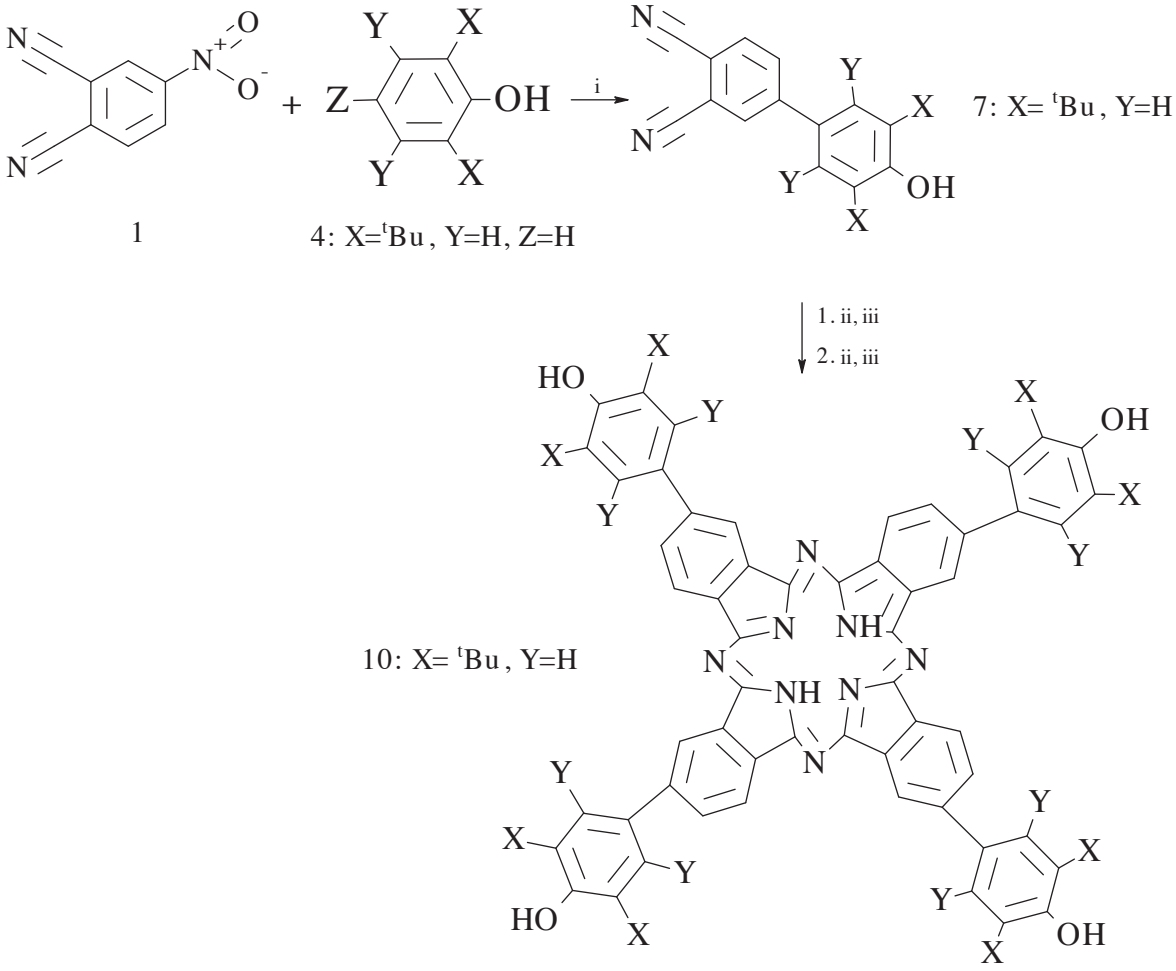
base-catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile **1** yielded the corresponding phenoxy-substituted phthalonitriles.[4,16] In DMF at room temperature each anion of the phenols (**2** and **3**) displaced the nitro group of **1** (Scheme 1); however, McKeown et al. reported that the anion of 2,6-di-*tert*-butylphenol **4** reacts efficiently with **1** as a carbon nucleophile to give **7** (Scheme 2).[16,17] We synthesized the 4-(3,5-dimethylphenoxy) phthalonitrile **5**, 4-(4-*tert*-butylphenoxy) phthalonitrile **6,**[18–21] and 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl) phthalonitrile **7** as starting materials for the derivatives of phthalocyanines. Compounds **5**, **6**, and **7** were obtained in moderate yield (52%, 47%, and 51%, respectively) by treating **1** with phenol derivatives (**2**, **3**, and **4**, respectively).



Scheme 1. Reagent and conditions for the synthesis of the phthalocyanines (**8** and **9**). i: Anhydrous K_2CO_3, DMF, 25 °C. 1. ii. Lithium, n-pentanol, 440 W, 138 °C, microwave, 10 min, iii. Acetic acid **(8a), (9a)**. 2. ii, Lithium, n-pentanol, 138 °C, 24 h, iii. Acetic acid **(8b), (9b)**.

The cyclotetramerization of phthalonitrile derivatives was performed in refluxing pentanol with Li, according to conditions previously reported.[16] We therefore decided to synthesize metal-free phthalocyanines with microwave irradiation, which can be more effective, faster, and energy efficient (**8a**, **9a**, and **10a**). In

addition, we compared those with others that were obtained via conventional heating methods (**8b**, **9b**, and **10b**). For a realistic comparison we repeatedly scrutinized the same parameters and conditions, including the solvents and base-catalyst (Scheme 1-2).



Scheme 2. Reagent and conditions for the synthesis of metal-free 2,9(10),16(17),23(24)-tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl) phthalocyanine (**10**). i: Anhydrous K_2CO_3, DMF, 48 h, 25 °C. 1. ii. Lithium, n-pentanol, 440 W, 138 °C, microwave, 10 min, iii. Acetic acid **(10a)**. 2. ii, Lithium, n- pentanol, 138 °C, 24 h, iii. Acetic acid **(10b)**.

The microwave experiments in the present study were performed in a CEM MARS5 microwave system (total power: 1200 W) equipped with an XP-1500 vessel. Using 440 W of power for irradiation, the temperature was raised to 138 °C and the reactions were completed in 10 min. We synthesized 3 metal-free phthalocyanines via microwave irradiation with a modification of a previously described method in which propylene glycol methyl ether acetate (PGMEA) as a solvent and DBU as a base-catalyst were used.[13]

Comparing the conventional and microwave irradiation methods, we observed very similar results (Table 1). All the reaction conditions were successfully repeated a few times and then, optimum results were taken into consideration. Compound **8** was obtained in 21.0% yield with the microwave irradiation method, versus

14.0% yield with the conventional method. The yield of **8a** via microwave irradiation was higher than that of the other microwave irradiation products. Compound **9** was obtained in 18.4% yield via the conventional method and in 16.0% yield with the microwave irradiation method.

Table 1. Comparison of the reaction methods.

	Compounds	Conditions (MW or Δ)	Time	T Temp. (°C)	Yield (%)	CHN calc.	CHN found
1	8a	MW	10 min	138	21.0	C: 77.24	C: 77.29
						H: 5.06	H: 4.63
						N: 11.25	N: 11.31
2	8b	Δ	24 h	138	14.0	C: 77.24	C: 73.76
						H: 5.06	H: 4.40
						N: 11.25	N: 10.86
3	9a	MW	10 min	138	16.0	C: 78.09	C: 76.86
						H: 6.00	H: 6.48
						N: 10.11	N: 9.89
4	9b	Δ	24 h	138	18.4	C: 78.09	C: 77.56
						H: 6.00	H: 6.58
						N: 10.11	N: 9.92
5	10a	MW	10 min	138	6.5	C: 79.36	C: 78.91
						H: 7.41	H: 8.42
						N: 8.41	N: 8.15
6	10b	Δ	24 h	138	6.7	C: 79.36	C: 78.50
						H: 7.41	H: 8.17
						N: 8.41	N: 8.03

Indeed, purification of **10** was very complicated. This compound has been previously synthesized only with the conventional method of McKeown et al.[16] They isolated this compound in 12% yield. In the present study we obtained it in 6.7 % yield with the conventional heating method and in 6.5% yield with the microwave irradiation method. We obtained the products in low yields because of the by products and the loss of purification.

In each case, spectroscopic analysis (UV-Vis and IR) and MALDI-TOF-MS spectroscopy gave spectra consistent with the proposed structures for products via microwave irradiation. The results of elemental analysis are shown in Table 1.

Cyclotetramerization of monosubstituted phthalonitriles usually results in the formation of 4 regioisomers. These 4 isomers posses C_{4h}, C_s, C_{2v}, and D_{2h} molecular symmetry.[16,22] Previously, Hanack et al. separated all 4 isomers of 2 different tetrasubstituted phthalocyanines by high pressure liquid chromatography (HPLC).[23,24]

UV-Vis absorption spectra of the metal-free phthalocyanines **8**, **9**, and **10** in chloroform exhibited the split Q band, which is characteristic of metal-free phthalocyanines (Figures 1-3).[16–21] The electronic spectra (UV-Vis) of phthalocyanines **8**, **9**, and **10** in chloroform are shown in Table 2. The phthalocyanines exhibited

the characteristic Q band in the visible region at 609-718 nm, which was attributed to the $\pi - \pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the macrocycle phthalocyanines ring, and the B band in the UV region at 300-400, which was due to the deeper π-levels$\rightarrow$LUMO transition.[25]

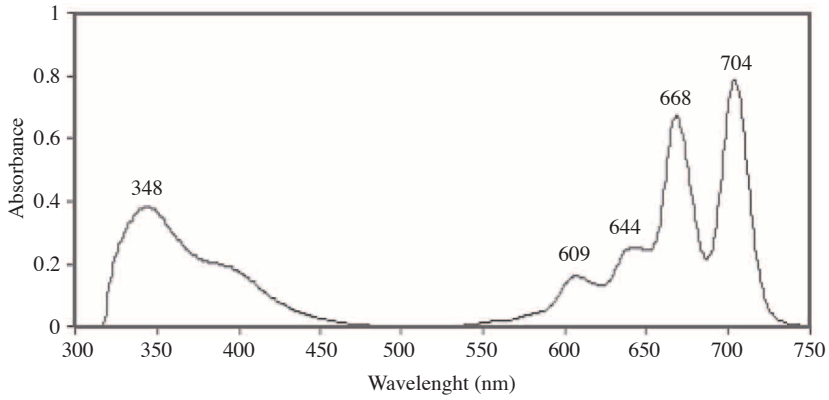


Figure 1. Absorption spectrum of metal-free 2,9(10),16(17),23(24)-tetra(3,5-dimethylphenoxy) phthalocyanine (**8**) in chloroform.

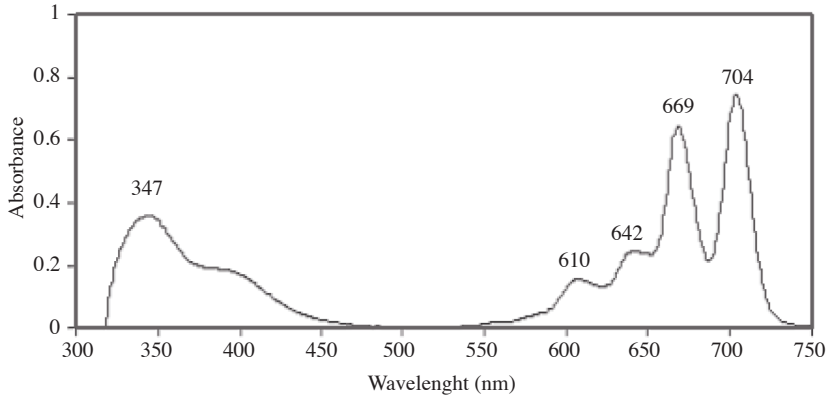


Figure 2. Absorption spectrum of metal-free 2,9(10),16(17),23(24)-tetra(4-*tert*-butylphenoxy) phthalocyanine (**9**) in chloroform.

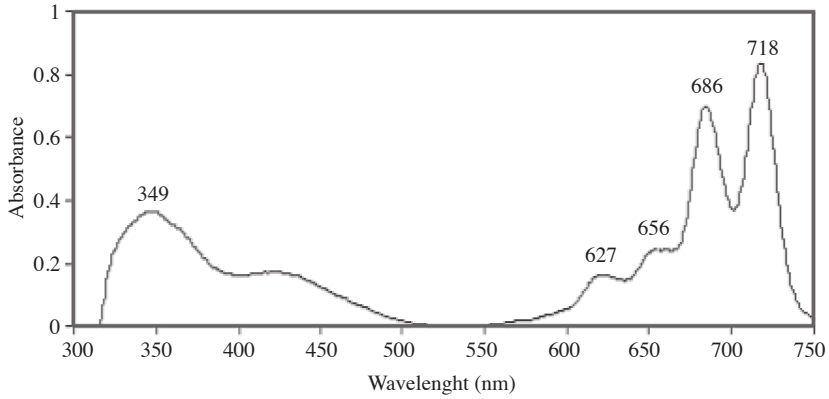


Figure 3. Absorption spectrum of metal-free 2,9(10),16(17),23(24)-tetra(3,5-di-*tert*-butyl-4-hydroxyphenyl) phthalocyanine (**10**) in chloroform.

The Pc derivatives showed good solubility in dichloromethane, chloroform, and DMF. Furthermore, compound **10** was soluble in methanol.

Table 2. Electronic spectra of the phthalocyanines (1×10^{-6} M) in $CHCl_3$.

Compounds	λ_{max}/nm (logε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$)				
8	348 (5.77),	609 (5.40),	644 (5.60),	668 (6.01),	704 (6.06)
9	347 (5.78),	610 (5.41),	642 (5.60),	669 (5.99),	704 (6.05)
10	349 (5.72),	627 (5.35),	656 (5.55),	686 (5.99),	718 (6.06)

The thermal stability of the compound **9** derivative was checked by TGA (Figure 4). The initial weight loss temperature and maximum weight loss temperature of the compound were about 540 and 549 °C (midpoint), respectively, while those for **8** were about 483 and 520 °C, and those for **10** were about 267 and 400 °C, respectively. These Pc-compounds underwent significant rapid weight loss at temperatures higher than 400 °C, indicating that phthalocyanine derivatives have high thermal stability.

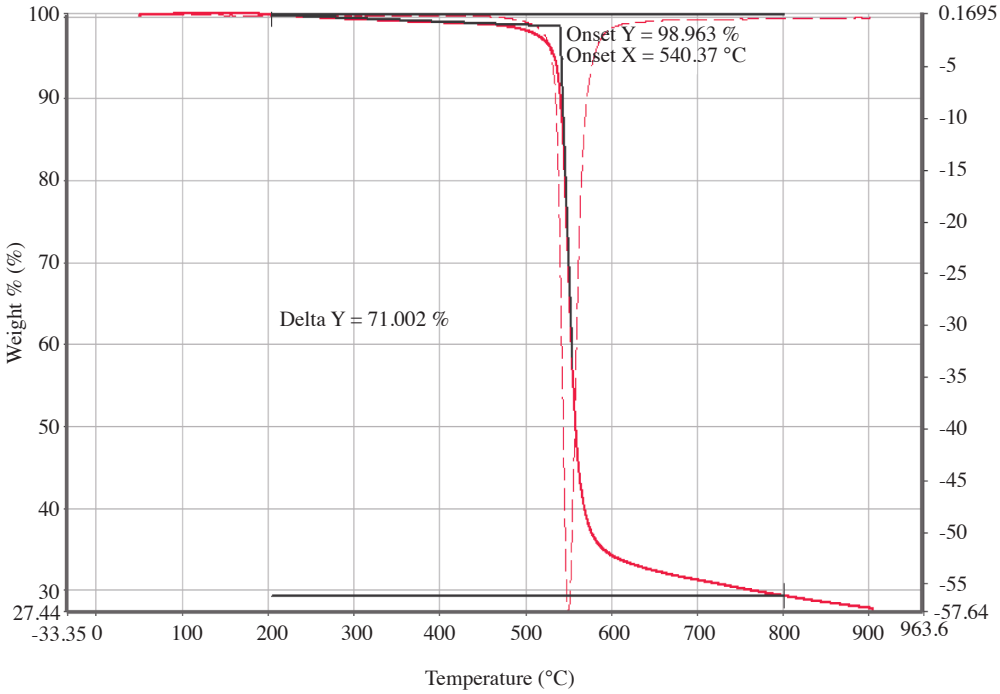


Figure 4. TGA curve of metal-free 2,9(10),16(17),23(24)-tetra(4-*tert*-butylphenoxy) phthalocyanine (**9**).

Conclusions

In the present study some substituted metal-free phthalocyanine derivatives were synthesized via microwave irradiation and conventional heating methods. Metal-free phthalocyanines are usually prepared by base-promoted cyclization of phthalonitriles. One of the typical procedures for conventional synthesis includes

treatment with Li metal in n-pentanol; however, in the present study, pentanol as a solvent and Li as a base-catalyst were used for the first time in the synthesis of metal-free phthalocyanine via microwave irradiation. The reactions were completed in 10 min with microwave irradiation, whereas the reactions were completed in 24 h with the conventional method. In addition, considering the total yield of **8**, the microwave irradiation method provided 1.5-fold higher product yield than the conventional heating method. For other products (**9, 10**), both of these methods gave similar yields. We obtained ultimate products in low yield because of repeated purification procedures.

The first 2 derivatives of phthalocyanine exhibited good solubility in dichloromethane, chloroform, and DMF. Additionally, compound **10** was soluble in methanol. UV-Vis absorption spectra of the metal-free phthalocyanines **8**, **9**, and **10** in chloroform exhibited the split Q band, which is characteristic of metal-free phthalocyanines (668 and 704 nm for **8**, 669 and 704 nm for **9**, and 686 and 718 nm for **10**) in chloroform; these results are similar to those previously reported.[25] The thermal stability of these Pc-compounds was very high; 520 °C (a maximum weight loss temperature) for **8**, 549 °C for **9**, and 400 °C for **10**, respectively.

Consequently, taking other data into consideration, these results suggest that the microwave irradiation method is better than the conventional method for the synthesis of these derivatives of phthalocyanine due to shorter reaction time and increased energy efficiency, yet with nearly the same or higher product yields.

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