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Araştırma Makalesi/Research Article

Characterization and Synthesis of Phthalocyanines Prepared from 4-(5-methyl-2-(2-phenylpropan-2-yl) cyclohexyloxy) phthalonitrile

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Abstract: A new the phthalonitrile derivative was synthesized from reaction of 4-nitrophthalonitrile with 5-methyl-2-(2-phenylpropan-2-yl) cyclohexanol. Phthalocyanines prepared from cyclotetramerization of this phthalonitrile in present metal salts. The products were purified by several techniques such as crystallization and washed with different solvents. These compounds were characterized by elemental analysis, IR, ^{1}H-and ^{13}C –NMR, UV-vis, MALDI-TOF mass spectral data
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Key words: Phthalonitrile derivative; Solubility; Magnesium; Metallophthalocyanine; Zinc.

4-(5-metil-2-(2-fenilpropan-2-il)siklohekziloksi)ftalonitrilden Hazırlanan Ftalosiyaninlerin Sentezi ve Karakterizasyonu

Özet: 5-metil-2-(2-fenilpropan-2-il)siklohekzanol ile 4-nitroftalonitrilin reaksiyonundan yeni bir ftalonitril türevi sentezlendi. Ftalosiyaninler metal tuzlarının varlığında bu ftalonitril türevinin siklotetramerizasyonundan hazırlandı. Ürünler kristallendirme ve farklı çözücülerle yıkama gibi birkaç teknikle saflaştırıldı. Bu bileşikler IR, ^{1}H-NMR, ^{13}C –NMR, UV-vis, MALDI-TOF kütle spektrumu ve elemental analiz ile karakterize edildi.

Anahtar kelimeler: Çinko; Çözünürlük; Ftalonitril türevi; Mağnezyum; Metalloftalosiyanin.

Introduction

Phthalocyanines have been a number of important industrial applications as dyes and pigments due to their bright blue or green colors combined with extraordinary thermal and photochemical stability (Leznoff & Lever, 1989). On the other hand, phthalocyanines and their derivatives display interesting electrical and electrochemical properties which are important for applications in chemical sensors, liquid crystals, catalysis, nonlinear optics, optical data storage and nanotechnology (Altun et al.,2008; Leznoff & Lever, 1993). Remarkable progress has been made in recent years in the use of pc derivatives as sensitizers for photodynamic therapy of cancer. A decisive disadvantage of pcs is their low solubility in organic solvents or water. The solubility can be increased, however, by introducing bulky or long chain groups, e.g. alkyl,alkoxy/alkylthio into the peripheral positions of the pc framework(Çamur &Bulut, 2010; McKeown, 1998). We have demonstrated that hexadeca tert-butyl substituents result with extremely soluble phthalocyanines in organic solvents (Ağırtaş,2008). In this study, synthesis, characterization and electrochemical of soluble phthalocyanines carrying at 5-methyl-2-(2-phenylpropan-2-yl) cyclohexyloxy substituents on the periphery are reported. This new class of substituted pcs usually exhibit high solubility in a number of organic solvents.

Experimental

Materials and methods

The starting compounds 5-methyl-2-(2-phenylpropan-2-yl) cyclohexanol and 4-nitrophthalonitrile were synthesized according to the published procedures (Caamaño et al., 2000; Young & Onyebuagu, 1990). All other 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(Perrin& Armarego , 1980). The solvents were stored over molecular sieves

(4Å). IR spectra were recorded on a Mattson 1000 FT-IR spectrometer in KBr pellets, electronic spectra on a Perkin Elmer Lambda 25 UV/Vis spectrophotometer. ^{1}H-NMR. spectra were recorded on a Bruker 200 MHz spectrometer with tetramethylsilane as internal standard.

Preparation of 4-(5-methyl-2-(2-henylpropan-2-yl) cyclohexyloxy) phthalonitrile (1)

4-Nitrophthalonitrile (1.73 g, 0.01 mol) was dissolved in DMF (25 ml) under nitrogen and 5-methyl-2-(2-phenylpropan-2-yl) cyclohexanol (2, 32 g, 0.01 mol) was added. After stirring for 15 min, finely ground anhydrous potassium carbonate (5.5 g, 0.04 mol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 24 h. Then the mixture was poured into 100 ml water, and extracted with dichloromethane (CH_2Cl_2). The crude product was washed first with 5 % $NaHCO_3$ and then with water and dried over anhydrous sodium sulfate. The product was evaporated to dryness. The product was recrystallized from ethanol. The yield was 1.17 g (33 %). mp 152-153 ^oC. Anal. Calc. for $C_{24}H_{26}N_2O$. C, 80.41; H, 7.31; N, 7.81; %. Found: C, 80.37; H, 7.33; N, 7.80 %. IR spectrum (cm^{-1}): 3057, 2966, 2945, 2922, 2842, 2229, 1596, 1500, 1477, 1458, 1368, 1326, 1254, 1127, 1087, 1020, 1001, 856, 841, 768, 703, 548, 526. ^{1}H NMR (DMSO-d$_6$): δ= 7.61- 7.56 (1H, d, Ar-H),7.27-7.17 (4H, s, Ar-H), 6.74-6.65 (3H, m, Ar-H), 4.17-4.06 (1H, m, aliphatic OCH_2), 2.22-1.48 (4H, m, aliphatic CH_2), 1.27 (4H, s, aliphatic CH_2), 1.65-0.99 (6H, d, CH_3 aliphatic), 0.95-0.91 (3H, d, CH_3 aliphatic). ^{13}C NMR (DMSO-d$_6$): δ= 160.2, 150.7, 135.1, 127.9, 125.5, 125.2, 119.7, 119.4, 117.2, 115.8, 115.4, 106.2, 79.2, 77.6, 77.0, 76.3, 51.5, 39.8, 39.7, 34.4, 31.2, 28.4, 26.5, 25.2, 21.7.

Preparation of tetrakis [(5-methyl-2-(2-phenylpropan-2-yl)cyclohexyloxy) phthalocyaninato] zinc (II) (2)

4-(5-methyl-2-(2-phenylpropan-2-yl)cyclohexy loxy)phthalonitrile (0.0895g, 0.25 mmol) and $ZnCl_2$ (0,0085 g) were dissolved in 1-hexanol(1.5 ml) under nitrogen and in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene(DBU) (0.05 ml) then heated with stirring at 160 ˚C for 24 h under N_2 atmosphere. The mixture was then cooled to room temperature and the reaction mixture product washed several times with water to dissolve any unreactive metal salt. Further purified chloroform was added in order to dissolve the crude product, which was then precipitated with ethanol. The product was filtered off, washed with ethanol and dried. The product is soluble in $CHCl_3$, CH_2Cl_2, acetone, tetrahydrofuran (THF), ethyl acetate and DMF.

The yield was 0.038 g (41 %). Anal. Calc. for $C_{96}H_{104}N_8O_4Zn$: C, 76.90; H, 6.99; N, 7.47; % Found C, 76.91; H, 6.97; N, 7.45 %. IR spectrum (cm^{-1}):2950, 2917, 1604, 1484, 1384, 1275, 1223, 1119, 1089, 1042, 993, 817, 746, 696. UV-Vis (chloroform): λ_{max}/nm: (10^{-5} ε dm^3 mol^{-1} cm^{-1}): 683 (5.09), 615 (4.40) and 355 (4.80). ^{1}H NMR (DMSO-d$_6$): δ= 7.27-7.26 (Ar-H), 4.11(OCH), 2.05-1.59(cyclo-protons), 1.26-1.21(aliphatic CH_2, CH_3). MALDI-TOF-MS m/z: 1498[M]$^+$.

Preparation of tetrakis[(5-methyl-2-(2-phenylpropan-2-yl)cyclohexyloxy) phthalocyaninat o] magnesium (II) (3)

4-(5-methyl-2-(2-phenylpropan-2-yl)cycloh exyloxy) phthalonitrile (0.0895 g, 0.25 mmol) and $MgCl_2$ (0,013 g) were dissolved in 1-hexanol (1.5 ml) under nitrogen and in the presence of 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) (0.05 ml). Then heated with stirring at 160 ˚C for 24 h under N_2 atmosphere. The mixture was then cooled to room temperature and the reaction mixture product washed several times with water to dissolve any unreactive metal salt. Further purified chloroform was added in order to dissolve the crude product, which was then precipitated with ethanol. The product was filtered off, washed with ethanol and dried. The product is soluble in $CHCl_3$, CH_2Cl_2, acetone, THF, ethyl acetate and DMF.The yield was 0.041 g (45 %). Anal. Calc. for $C_{96}H_{104}MgN_8O_4$: C, 79.07; H, 7.19; N, 7.68; % Found C, 79.10; H, 7.17; N, 7.70 %. IR spectrum (cm^{-1}): 2924, 1617, 1485, 1244, 1093, 1045, 998, 763, 699, 617, 481. UV-Vis (chloroform): λ_{max}/nm: (10^{-5} ε dm^3 mol^{-1} cm^{-1}): 683 (5.45), 616 (4.81) and 352 (5.26). ^{1}H NMR ($CDCl_3$): δ= 7.26-7.22 (Ar-H), 4.10 (OCH), 2.17-2.05 (cyclo-protons), 1.61-1.19 (aliphatic CH_2, CH_3). MALDI-TOF-MS m/z: 1459[M]$^+$.

Results and Discussion

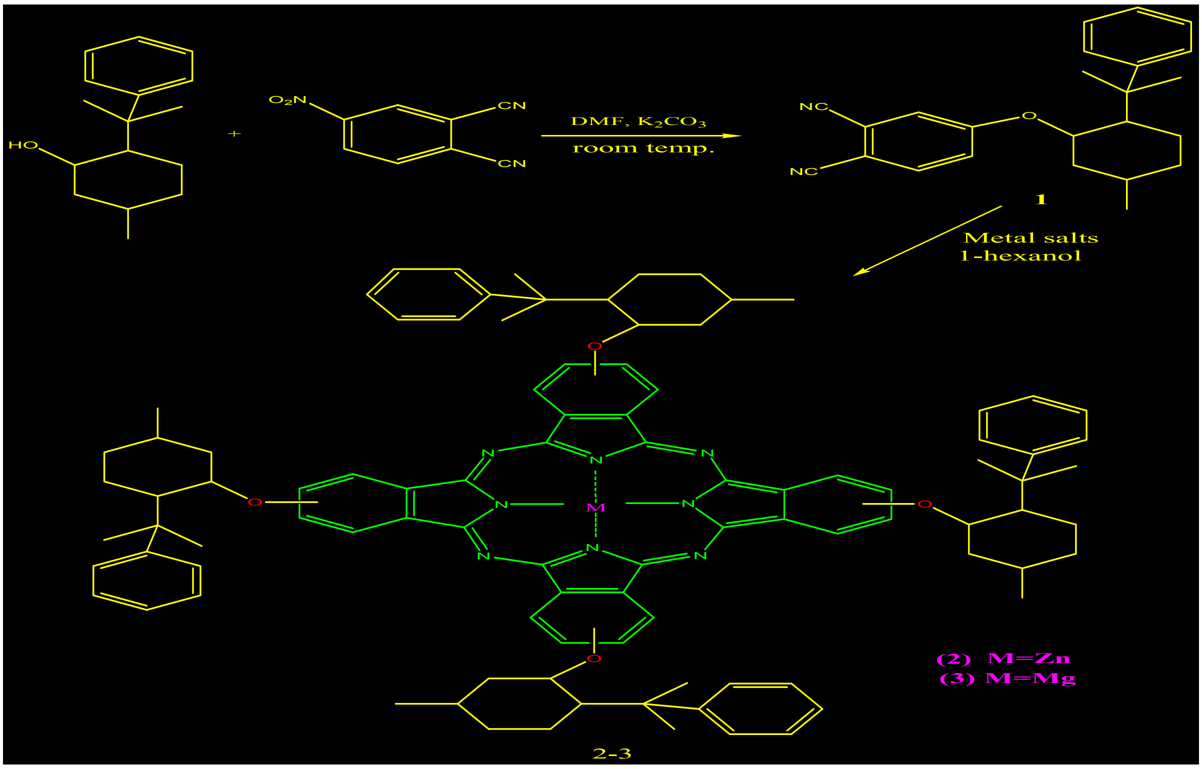
The mode of preparation of 4-(5-methyl-2-(2-phenylpropan-2-yl) cyclohexyloxy) phthalonitrile **1** and metallophthalocyanines **2-3** are shown in Scheme 1. Compound **1** was accomplished by a base-catalysed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with 5-methyl-2-(2-phenylpropan-2-yl) cyclohexanol. The reaction was carried out at room temperature in dimethylformamide with K_2CO_3 as the base, and under nitrogen atmosphere. The metallophthalocyanines **2-3** were synthesized in 1-hexanol in the presence of a few drops of 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) as a strong base at reflux temperature under nitrogen atmosphere. Tetra (5-methyl-2-(2-phenylpropan-2-yl) cyclohexyloxy) substituted Pcs **(2-3)** showed enhanced solubility in a number of organic solvents, e.g. dichloromethane, chloroform, acetone, ethyl acetate, tetrahydrofuran, dimethylformamide.

Characterization of the compounds involved a combination of methods including elemental analysis, ^{1}H and ^{13}C-NMR, UV-vis, IR. spectra and mass spectroscopy.

Spectral data of the original synthesized compounds are consistent with the proposed structures. Comparison of the IR spectral data clearly indicated the formation of compound **1**, the appearance of new absorption bands at 2966-2945 cm^{-1}(CH_3), 2922-2842 cm^{-1}(CH_2), 2229 cm^{-1}(C≡N), 1254 cm^{-1}(Ar-O-Ar). After conversion of the compound **1** into the phthalocyanines (**2-3**), the sharp peak for the C≡N vibration around 2229 cm^{-1} disappeared. The ^{1}H-NMR spectrum of **1** exhibited aromatic protons (Ar-H) at 7.61-6.65 ppm, at 4.17-4.06 ppm (OCH), at 2.22-1.27 ppm (CH_2, CH_3) and at 1.65-0.99 ppm (CH_3). The ^{1}H-NMR spectrum of **1** is in accord with expected structure and indicates the C-O at 160, the nitrile carbons at 115.8, 115.4, the CH_3 at 21.7 for **1**.

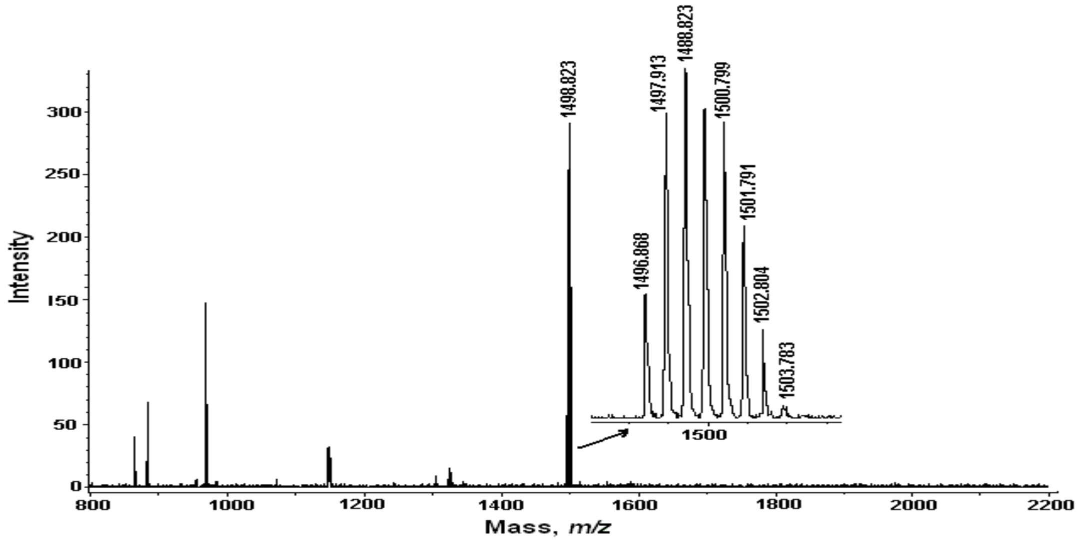
The ^{1}H-NMR spectra of phthalocyanines **2-3** were almost identical except for small shift. The ^{1}H-NMR spectra of **2-3** exhibited aromatic protons (Ar-H) at 7.27-7.26 ppm (for **2**), 7.26-7.22 ppm (for **3**), at 4.11 ppm (OCH) (for **2**), at 4.10 ppm (OCH) (for **3**), at 2.05-1.59 ppm (CH_2,CH_3) (for **2**)and at 1.26-1.21 ppm (CH_3) (for **2**), at 2.17-2.04 ppm (CH_2,CH_3) (for **3**) and at 1.61-1.19 ppm (CH_3) (for **3**).

A closed investigation of the mass spectra of the phthalocyanines confirmed the proposed structure. The MALDI-TOF-MS measurements of the compounds **2** and **3** gave the characteristic molecular ion peaks at m/z: 1498[M]$^+$ (Fig.1) and m/z: 1459[M]$^+$ respectively by which the proposed structures were confirmed.



Scheme1. Synthetic pathway of 4-(5-methyl-2-(2-phenylpropan-2-yl) cyclohexyloxy) phthalonitrile (**1**) and phthalocyanines (**2-3**)

Figure 1. MALDI-MS spectrum of **2**The phthalocyanines **2-3** show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300-350 nm (B band) and the other in the visible part of the spectrum around 600-700 nm (Q band). UV-vis spectra of the phthalocyanine **2** and **3** in $CHCl_3$ was displayed typical



absorptions around 683, 615 nm and 683, 616 nm in the Q band region, respectively (Fig.2). The Q band was attributed to the π→π* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. Other bands (B) in UV region at 355 nm and 352 nm were observed due to transition from the lower π levels to the LUMO. (Leznoff & Lever, 1993).

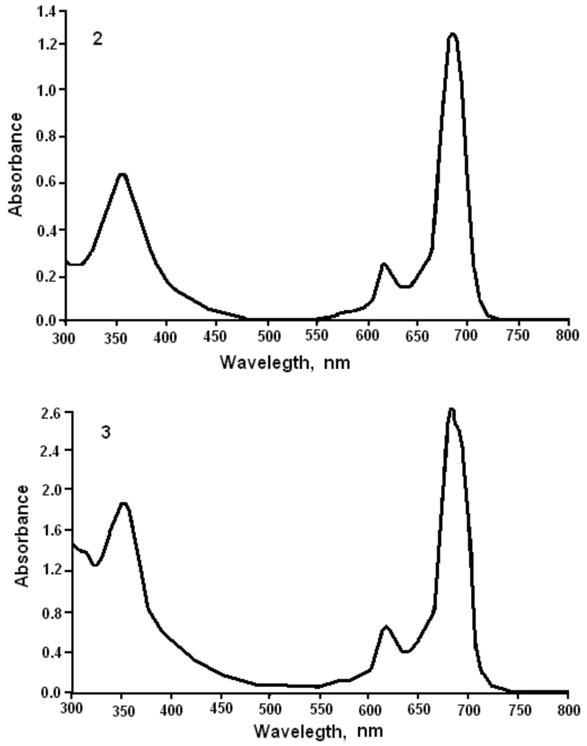


Figure 2. Absorption spectra of **2-3** in chloroform

Conclusion

We have successfully synthesized and characterized new metallo- phthalocyanines substituted with four 5-methyl-2-(2-phenylpropan-2-yl) cyclohexyloxy substituents on peripheral positions.These compounds are soluble in number of organic solvents, e.g. dichloromethane, chloroform, acetone, ethyl acetate, tetrahydrofuran

These results allow us to consider high soluble metallophthalocyanines (**2-3**) as promising second-generation photosensitizers for photobiologicall purposes.

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