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Synthesis, Characterization, and Investigation of the Spectroscopic Properties of Novel Peripherally 2,3,5-trimethylphenoxy Substituted Cu and Co Phthalocyanines, Computational and Experimental Studies of 4-(2,3,5-trimethylphenoxy)phthalonitrile

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Abstract: 4-(2,3,5-trimethylphenoxy)phthalonitrile (**3**) was prepared via aromatic nucleophilic substitution reaction and characterized by FT-IR, mass spectrometry, ^{1}H and ^{13}C NMR techniques. The molecular structure of compound (**3**) was optimized using Density Functional Theory (DFT/B3LYP) method with 6-311G(d,p) basis set in the ground state. The molecular geometric parameters which were obtained by X-ray single crystal diffraction method and the spectral results were compared with computed bond lengths and angles, vibrational frequencies, and ^{1}H, ^{13}C NMR chemical shifts values of compound (**3**). Also, Cu(II) and Co(II) phthalocyanines were synthesized by the treatment of dinitrile derivative with anhydrous $CuCl_2$ or $CoCl_2$ under N_2 atmosphere in dry n-pentanol at 140 °C. The new compounds have been determined by elemental analysis, FT-IR, and electronic absorption. The UV-Vis spectra of the Cu(II) and Co(II) phthalocyanines were recorded with different concentration in THF and also with different solvents as DMF, DMSO, DCM, $CHCl_3$, toluene.

Keywords: Phthalocyanines, phthalonitrile, 2,3,5-trimethylphenol, DFT.

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INTRODUCTION

Phthalocyanines (Pcs), discovered accidentally in 1907 and characterized in 1930s, are synthetic heterocyclic aromatic compounds [1]. Pcs have high thermal and chemical stability along with their unique properties such as strong visible light absorption, high molar absorption coefficients, electron transfer abilities, and the flexibility involved in the synthesis of these compounds [2]. These features promote an extensive use of these molecules primarily as dyes and pigments. A minimum amount of 80.000 tons of Pcs are produced per year just for this purpose [3]. They have been also used in other applications such as liquid crystals [4, 5], optical applications [6, 7], HIV inactivation [8, 9], electrochromism [10, 11], molecular solar cells [12, 13], chemical sensors [13, 14], semiconductors for organic field-effect transistors [16, 17], and photodynamic therapy [18, 19, 20].

These applications of the phthalocyanines can not be achieved since many unsubstituted Pcs are not soluble neither in organic solvents nor in water. The solubility can be increased by adding substituents to the periphery, nonperiphery or axial position of phthalocyanines, and designing central metal ions differently. It is well known that tetrasubstituted phthalocyanines usually present a higher solubility than octasubstituted Pc derivatives [21, 22, 23].

Our earlier studies concentrated on synthesis and characterization of metal-free and metallophthalocyanines containing tetrathiaoxa [24], dithiaoxa [25], diazadithiaoxa macrocyclic moieties [26], N-(n-octyl)mercaptoacetamide groups [22], naphthalene-amide groups [27] and 3,5-dimethoxyphenol groups [28]. The present work introduces the preparation and characterization of Cu(II) and Co(II) phthalocyanines containing 2,3,5-trimethylphenol moieties. Then UV-Vis spectra of these compounds were recorded in different solvents and different concentrations. Furthermore, molecular geometry parameters, vibrational frequencies and ^{1}H, ^{13}C NMR chemical shift values of the 4-(2,3,5-trimethylphenoxy)phthalonitrile, which was reported the crystal structure of which was reported by our group in previous paper [29], were calculated and compared with the experimental specifications.

MATERIALS AND METHODS

IR spectra was recorded on a Perkin Elmer Frontier FT-IR Spectrometer as KBr pellets. UV-Vis spectra were recorded on a Perkin Elmer Lambda 35 UV/Vis Spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on an Agilent 600 MHz spectrometer (Çankırı Karatekin University NMR Laboratory). Mass spectra were measured on an Ab Sciex 3200 QTrap LC-MS/MS (Amasya University-AUMAULAB). Elemental analyses were performed on a Leco

Truspect Micro Analyzer. 4-Nitrophthalonitrile was synthesized by following the procedure reported in [30]. All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. DMF was dried and purified as described by Armarego and Perrin [31]. The homogeneity of the products was tested by TLC (SiO_2).

Computational Details

The crystal structure of the compound was (**3**) reported by Akbal *et al*. [29], so the molecular geometry was taken on the coordinates obtained from the X-ray single crystal diffraction data. The geometry optimization was carried out with DFT / B3LYP (Becke's Three Parameter Hybrid Functional using the Lee, Yang, and Parr Correlation Functional) [32-34] method and 6-311G(d,p) the basis set in the ground state. All the computational process was realized over the optimized structure and the same method. The harmonic vibrational frequencies were computed and multiplied by the scale factor 0.9682 [35] to eliminate systematic errors between the experimental values and theoretical values the frequencies. ^1H and ^{13}C-NMR chemical shift values were calculated according to GIAO (Gauge-Independent Atomic Orbital) method [36] and with respect to TMS (tetramethylsilane) an internal standard chemical shifts as solvent $CDCI_3$. The predicted ^1H-NMR and ^{13}C-NMR chemical shifts were obtained from the equation $\delta=(\Sigma TMS-\Sigma)$, where δ is the chemical shift, Σ is the absolute shielding and ΣTMS is the absolute shielding of the standard (TMS), its values are 32.002 and 184.923 ppm, respectively. All the computational analysis on the structure have been performed with Gaussian 09W [37] electronic structure and GaussView 5.0 [38] graphical interface software on a Intel Core i5/3.2 GHz personal computer.

Synthesis

Synthesis of 4-(2,3,5-trimethylphenoxy)phthalonitrile (3): The compound (**3**) was synthesized according to the reported procedure [29]. FT-IR :ν_{max}, cm^{-1} 3091 (Ar-CH), 2965, 2947, 2917, 2860 (CH_3), 2231 (CN), 1597 (C=C), 1566 (C=C), 1495, 1454, 1408, 1380, 1371, 1312, 1278 (C-O), 1244, 1199, 1162, 1133, 1088, 1069, 1022, 971, 946, 870, 856, 842, 746, 717, 726, 661. ^1H NMR (600 MHz, $CDCl_3$, δ, ppm) 2.00 (s, 3H, methyl), 2.30 (s, 6H, methyl), 6.64 (s, 1H, Ar-H), 6.95 (s, 1H, Ar-H), 7,15 (s, 1H, Ar-H), 7.17 (d, *J* = 1.6, 1H, Ar-H), 7.69 (d, *J* = 8.2, 1H, Ar-H). ^{13}C NMR (151 MHz, $CDCl_3$):δ, ppm 11.82 (CH_3), 19.96 (CH_3), 20.83 (CH_3), 108.14, 115.08, 115.49 (CN), 117.60 (CN), 118.92, 120.52, 120.64, 125.55, 128.91, 135.35, 137.24, 139.54, 151.18, 162.05. MS m/z [M+H$^+$] 262.8

General procedure for the synthesis of copper and cobalt phthalocyanines: The mixture of 4-(2,3,5-trimethylphenoxy)phthalonitrile (0.75 g, 2.88 mmol), the related anhydrous metal salt [$CuCl_2$ (0.15 g, 1,12 mmol) for compound **4**, $CoCl_2$ (0.14 g, 1.06 mmol) for compound **5**] and 0.5 mL DBU was heated at 140 °C with dry n-pentanol (10 mL) and stirred for 28 h in a nitrogen atmosphere. Then, the mixture was cooled to room temperature, precipitated by adding methanol and filtered off. The green products were washed with hot methanol, hot ethanol, diethyl ether, and water. They were washed with methanol for 24 h in the soxhlet apparatus and dried *in vacuo*.

2(3), 9(10), 16(17), 23(24)-Tetrakis-(2,3,5-trimethylphenoxy) copper(II) phthalocyanine (4)

The product is soluble in DMF, DMSO, DCM, toluene, $CHCl_3$, and THF. Yield: 0.689 g (86%); mp> 250°C; anal. calcd. for $C_{68}H_{56}N_8O_4Cu$: C, 73.40; H, 5.07; N, 10.07%. Found: C, 73.45; H, 5.08; N, 10.11%. FT-IR :ν_{max}, cm^{-1} 3064 (Ar-CH), 2916, 2859, 1611, 1575, 1506, 1470, 1403, 1342, 1294, 1268, 1224, 1174, 1133, 1120, 1094, 1076, 1049, 948, 970, 853, 823, 747, 666.

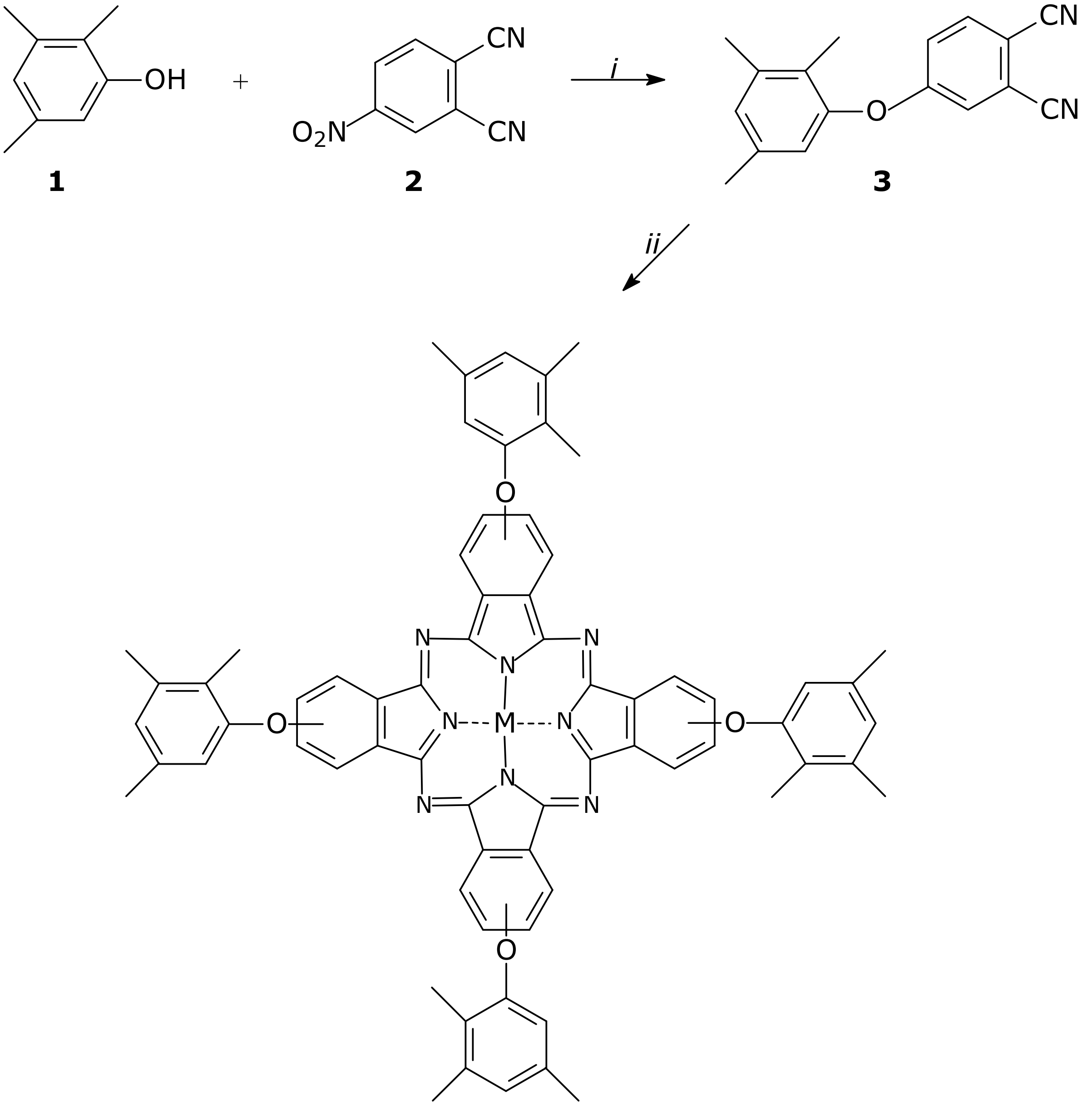
2(3), 9(10), 16(17), 23(24)-Tetrakis-(2,3,5-trimethylphenoxy) cobalt(II) phthalocyanine (5)

The product is soluble in DMF, DMSO, DCM, toluene, $CHCl_3$, and THF. Yield: 0.459 g (58%); mp > 250°C; anal. calcd. for $C_{68}H_{56}N_8O_4Co$: C, 73.70; H, 5.09; N, 10.11%. Found: C, 73.75; H, 5.10; N, 10.06%. FT-IR :ν_{max}, cm^{-1} 3064 (Ar-CH), 2918, 2863, 1612, 1575, 1524, 1473, 1408, 1332, 1294, 1269, 1226, 1177, 1123, 1094, 1078, 970, 955, 855, 824, 752, 665.

RESULTS AND DISCUSSION

Synthesis and characterization

Scheme 1 shows the synthetic route to tetrakis(2,3,5-trimethylphenoxy) Cu and Co phthalocyanines. 4-(2,3,5-trimethylphenoxy)phthalonitrile (**3**) was firstly prepared by treating 4-nitrophthalonitrile (**2**) with 2,3,5-trimethylphenol in DMF using K_2CO_3 as the base for nucleophilic displacement reaction and gave high yield (74 %) [29]. Copper(II) and cobalt(II) phthalocyanines (**4** and **5**) were synthesized by the treatment of compound **3** with anhydrous $CoCl_2$ and $CuCl_2$ in n-pentanol in the presence of 0,5 mL 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a strong base at 140 °C for 28 h in a nitrogen atmosphere. The yields of compounds **4** and **5** were 86% and 58%, respectively.



Scheme 1. Synthetic route for compounds (**4** and **5**) i: DMF, K_2CO_3, N_2, 40°C, 48h ii: n-pentanol, DBU, $CuCl_2$ or $CoCl_2$, N_2, 24h, 140°C.

The phthalocyanines showed high solubility in organic solvents such as DMF, DMSO, DCM, toluene, $CHCl_3$, and THF, but they are insoluble in methanol, ethanol, and diethyl ether. The products having been washed consequently with different solvents were obtained in sufficient purity. All new compounds were characterized by UV-Vis, FT-IR, ^{1}H NMR, ^{13}C NMR, MS spectra, and elemental analysis. All the results were in very good agreement with targeted structures.

In the FT-IR spectrum of starting compound (**3**), aromatic CH, aliphatic CH, nitrile C≡N, aromatic C=C, ether Ar-O-Ar stretching vibrations appeared at 3091, 2964, 2231, 1597, and 1278 cm^{-1}, respectively. While the strong -C≡N band appeared at 2231 cm^{-1}, this band completely disappeared after conversion to compounds (**4** and **5**). The FT-IR spectra phthalocyanines are very similar with the exception of small stretching shifts. ^{1}H NMR and ^{13}C NMR spectra of phthalocyanines (**4** and **5**) could not be measured due to the paramagnetic cobalt(II) and copper(II) centers.

Ground state electronic absorption spectra

The phthalocyanines can be characterized by recording UV-Vis spectra. These compounds have two strong absorption regions, one of them in the UV region at *ca*. 275-400 nm (B band) and the other in the visible region at 600-700 nm (Q band) [2]. The UV-Vis spectra of the phthalocyanines (**4**, **5**) were recorded in different solvents (Figures 1 and 2). The data were presented in Table 1.

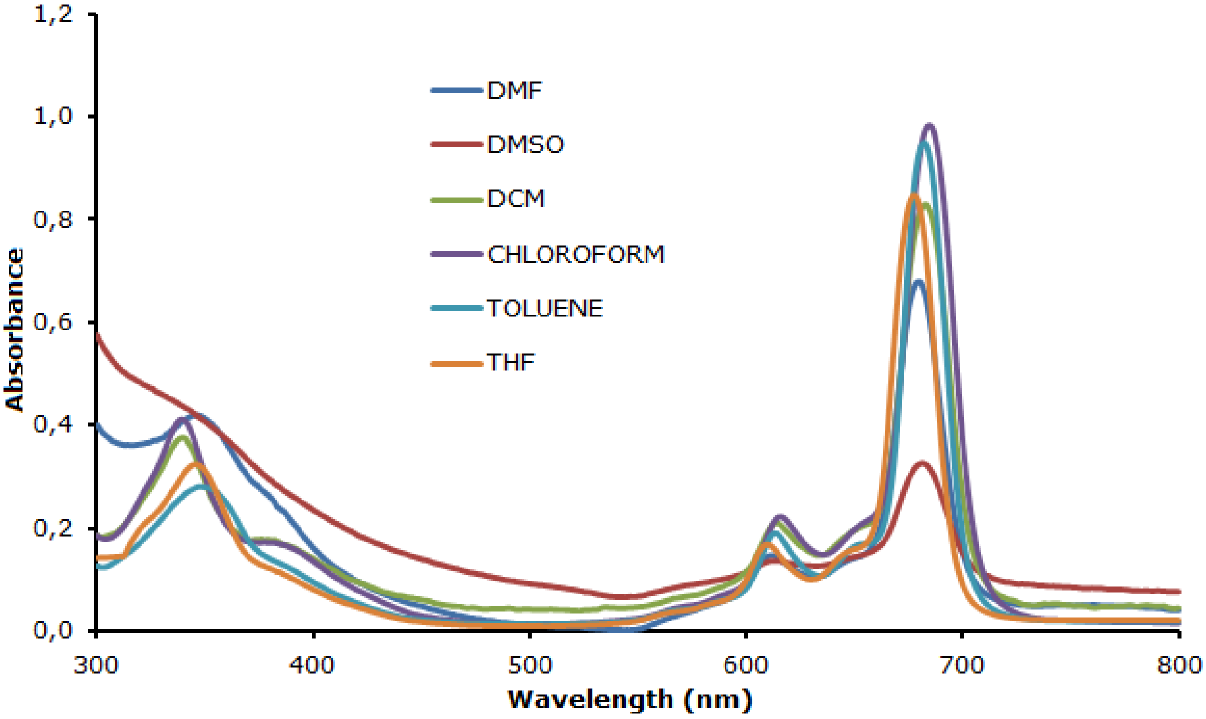


Figure 1. Absorption spectra of the compound (**4**) (CuPc) in different solvents.

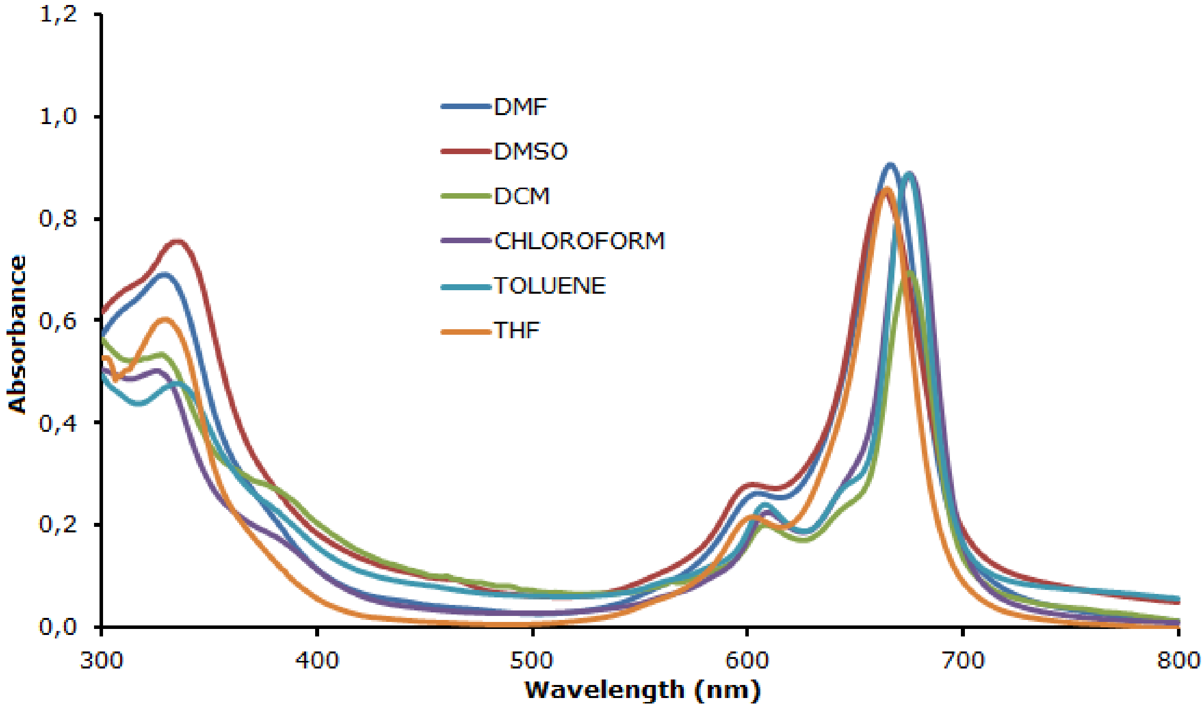


Figure 2. Absorption spectra of the compound (**5**) (CoPc) in different solvents.

The phthalocyanines (**4**, **5**) showed monomeric behavior in different solvents, evidenced by a single (narrow) Q-band at 678-685 nm for **4,** 663-675 nm for **5**, confirming non-aggregation. However compound (**4**) showed aggregation in DMSO (Figure 1). B-Band absorptions in different solvents were observed at 339-348 nm for **4** and 326-335 nm for **5**.

Figures 2 and 4 show electronic absorption spectra of Pcs (**4** and **5**) in the concentration range $2x10^{-6}$ - $1.20x10^{-5}$ M in THF. As shown in the Figures 3 and 4, the Q band increases in intensity with increasing concentration of phthalocyanines (**4** and **5**) and no new band was observed due to the aggregated species [39, 40]. Beer's law was obeyed for (**4**) and (**5**) in the concentration range $2x10^{-6}$ - $1.20x10^{-5}$ M.

Table 1. UV-Vis spectral data for phthalocyanines (**4** and **5**) in various solvents at a concentration of 1x10^{-5} M

Compound	Solvent	Q-Band		B-Band	
		λ_{max} (nm)	ε (dm^3 mol^{-1} cm^{-1})	λ_{max} (nm)	ε (dm^3 mol^{-1} cm^{-1})
4	DMF	680, 612	67880; 14690	346	41930
4	DMSO	681, 613	32630; 13620	340	43640
4	DCM	683, 614	82930; 20920	339	37480
4	$CHCl_3$	685, 616	98130; 22150	339	41080
4	Toluene	682, 613	94860; 18930	348	27980
4	THF	678, 610	84600; 16810	346	32370
5	DMF	666, 605	90500; 26370	329	69040
5	DMSO	663, 603	85070; 28070	335	75500
5	DCM	675, 608	69280; 20100	328	53310
5	$CHCl_3$	675, 609	88700; 22660	326	50320
5	Toluene	675, 608	88680; 24020	334	47740
5	THF	665, 603	85890; 21770	330	60360

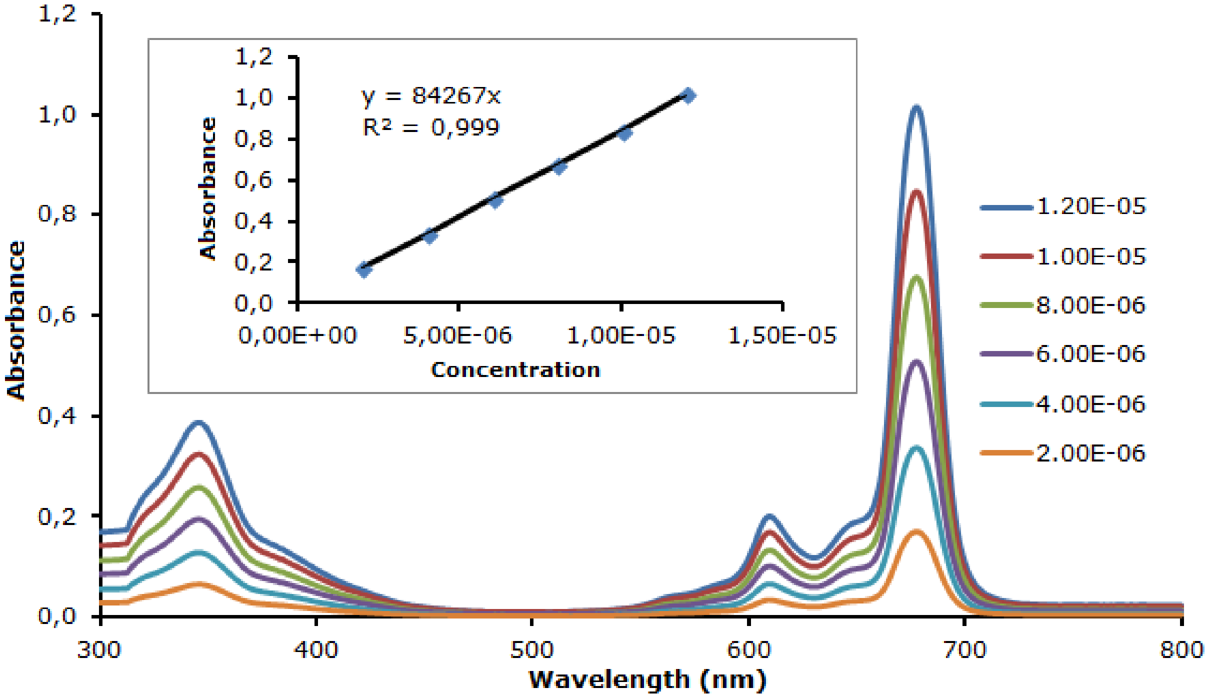


Figure 3. Absorption spectra of the compound (**4**) (CuPc) in THF at different concentrations.

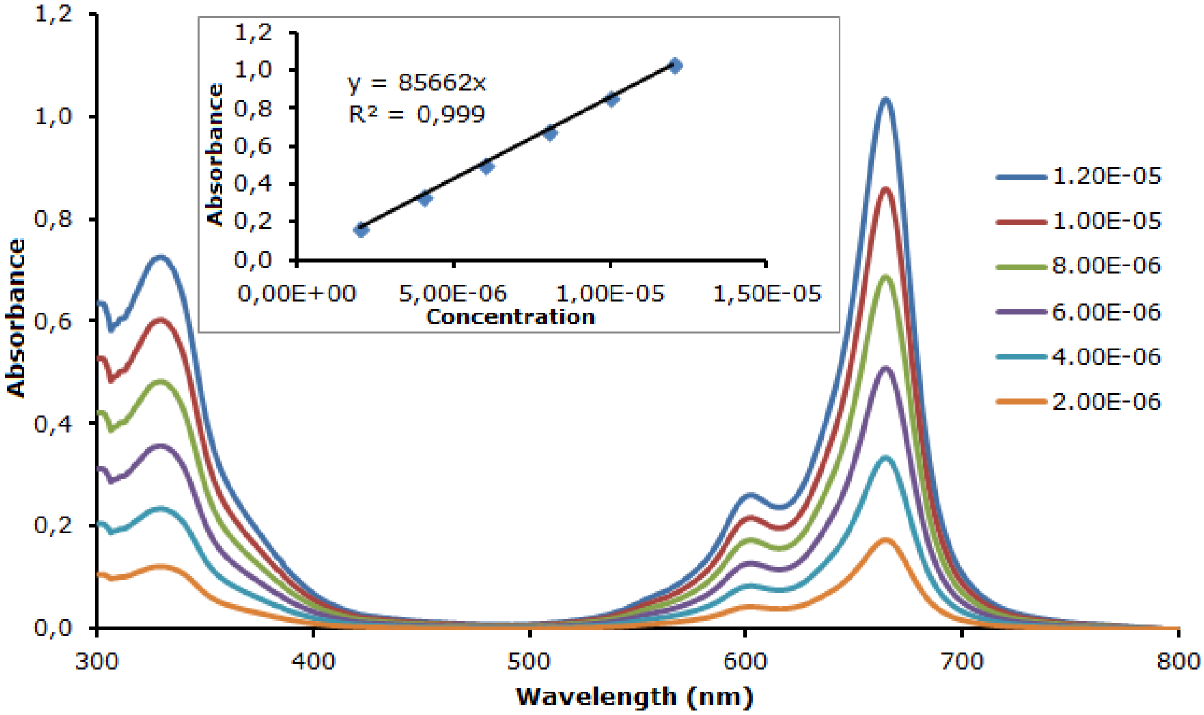


Figure 4. Absorption spectra of the compound (**5**) (CoPc) in THF at different concentrations.

Optimized Structure

The experimental geometric structure with the atom-mumbering scheme [29] and the optimized structure of the compound (**3**) are shown in Figure 5. The crystal structure of the compound (**3**) has an orthorhombic crystal system and Pbcaspace group with *a*=7.8929 (8) Å, *b*=29.415 (4) Å, *c*=12.4679 (14) Å, V=2894.7 (6) Å^3 and *Z*=8 unit cell parameters [31]. Some selected optimized structure parameters such as bond lengths and angles, torsion angles were compared with experimental values and the results were tabulated in Table 2.

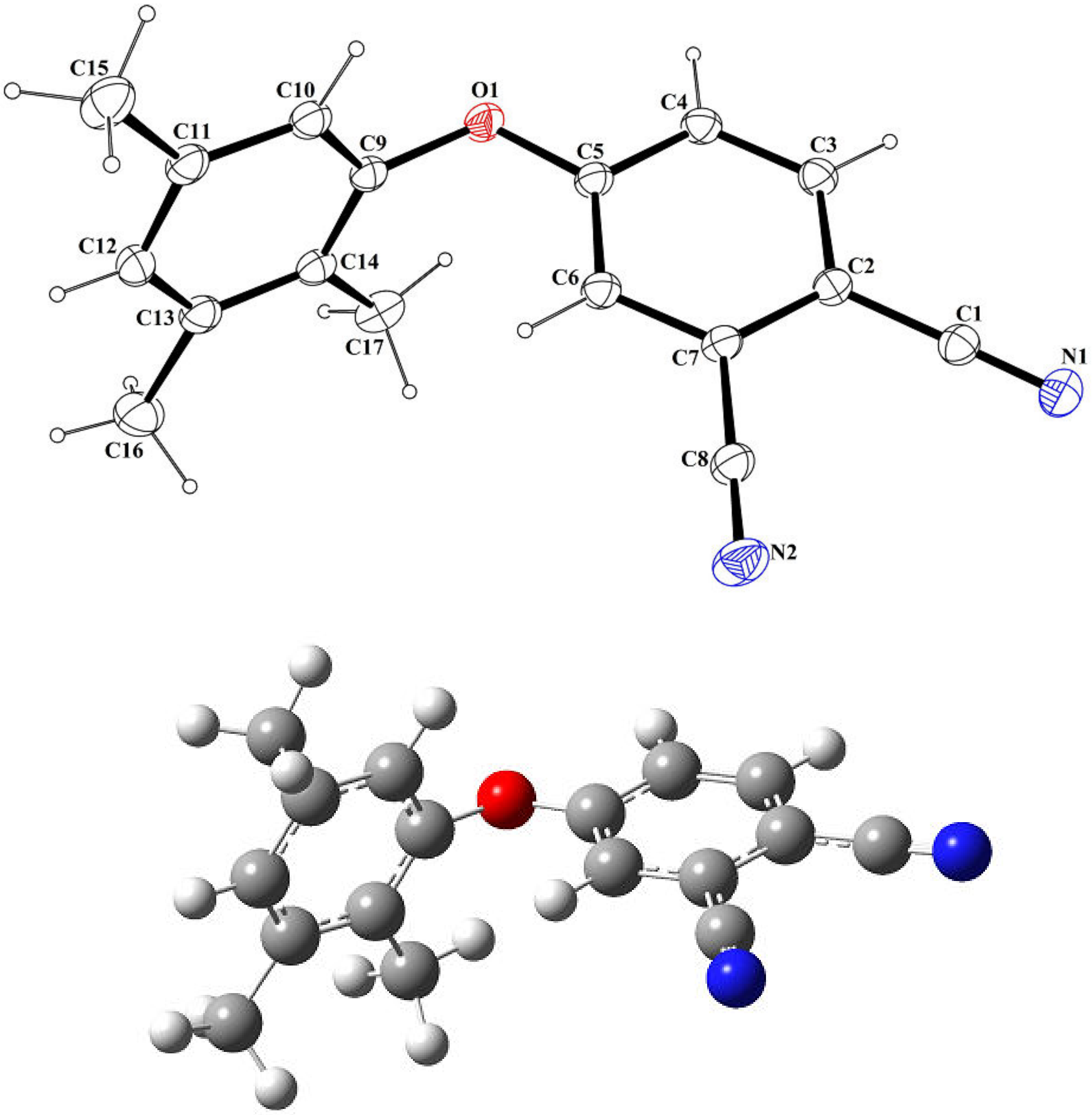


Figure 5. Top: An ORTEP-III view of the structure of the compound (**3**), showing 30% probability displacement ellipsoids and the atom-mumbering scheme [31]. **Bottom:** The optimized geometric structure of the compound (**3**) with DFT/B3LYP method and 6-311G(d,p) basis set.

Table 2. Some experimental and optimized geometrical parameters of the compound (**3**).

Parameters	**Experimental Values Ref.[31]**	**Theoretical Values DFT/B3LYP/6-311G(d,p)**
Bond lengths (Å)		
C1—N1	1.142(2)	1.155
C1—C2	1.433(3)	1.426
C7— C8	1.439(2)	1.430
C8—N2	1.134(2)	1.154
C2—C3	1.393(2)	1.402
C3—C4	1.371(2)	1.382
C5—O1	1.362(19)	1.359
C9—O1	1.410(19)	1.403
C11—C15	1.508(2)	1.509
C13—C16	1.520(3)	1.509
C14—C17	1.503(3)	1.507
Bond angles (°)		
N1—C1—C2	179.27(2)	178.42
N2—C8—C7	179.12(2)	178.50
C5—O1—C9	118.22(12)	120.05
C4—C5—O1	116.14(14)	115.99
C10—C9—O1	116.97(18)	117.99
C9—C14—C17	121.25(18)	121.60
C10—C11—C15	121.71(2)	121.27
Torsion angles (°)		
N1—C1—C2—C3	-122.21(17)	0.384
N2—C8—C7—C6	-66.13(14)	-0.030
C4—C5—O1—C9	-179.82(16)	-172.13
C10—C9—O1—C5	96.18(18)	77.32

As seen in Table 2, C1-N1, C8-N2 bond lengths are 1.142, 1.134 Å accordingly X-ray analysis data, 1.155, 1.154 Å for DFT/B3LYP/6-311G(d,p) method. These lengths were stated as 1.142 Å experimentally, 1.162 Å for 6-31G(d) [41], 1.138 experimentally, 1.146 Å for 6-31G(d,p) basis sets [42] in other DFT studies containing phthalonitrile group, and results are in agreement with typical carbon-nitrogen triple bond (about 1.16 Å). The lengths of carbon-oxygen bond which serves as a bridge between phthalonitrile and trimethylbenzene groups are 1.359 and 1.403 Å, theoretically, 1.36, 1.44 Å for 6-31G(d) basis set in another study [43]. Also N1-C1-C2, N2-C8-C7 bond angles of phthalonitrile are 178.42, 178.50° while these values are recorded 178.24, 178.51°for 6-311+G(d,p) basis set in a similar paper [44].

When the experimental values compared with theoretical values, minor discrepancy are observed between them, because compound is accepted in the gas phase during theoretical calculation process, whereas it is solid phase in the experimental analysis. Even so, correlation coefficient is 0.9984 for bond lengths, 0.9996 for bond angles and according to these values it can be said that it showed a good correlation. Also, an atom-by-atom superimposition of the structure the compound (**3**) as established by DFT/B3LYP/6-311G(d,p) and X-ray data is shown in Figure 6 and RMSE value is 0.277 Å.

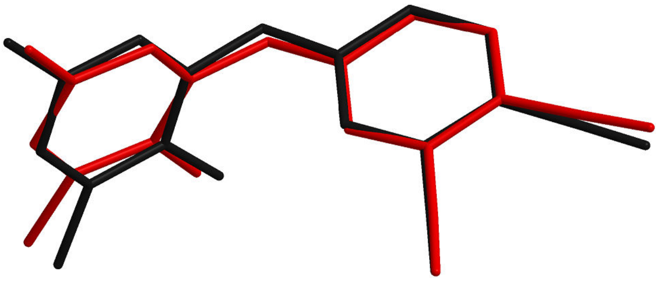


Figure 6. Atom-by-atom superimposition of the calculated structure (DFT/B3LYP76-311G(d,p) (red) on the X-ray structure (black) of the compound (**3**).

Vibrational Spectral Analysis

The scaled harmonic vibrational frequencies of the compound (**3**) were calculated with DFT/B3LYP/6-311G(d,p) basis set. The compound (**3**), which has 34 atoms and 96 fundamental vibrational frequencies, consisting of phthalonitrile and trimethylbenzene groups. The theoretical vibrational assignments in these groups were designated with Gauss View interface program [38] and compared with spectral values and the results were tabulated in Table 3. Also, the FT-IR spectrum which was plotted on the transmittance (%) against the wavenumber (cm^{-1}) is shown in Figure 7.

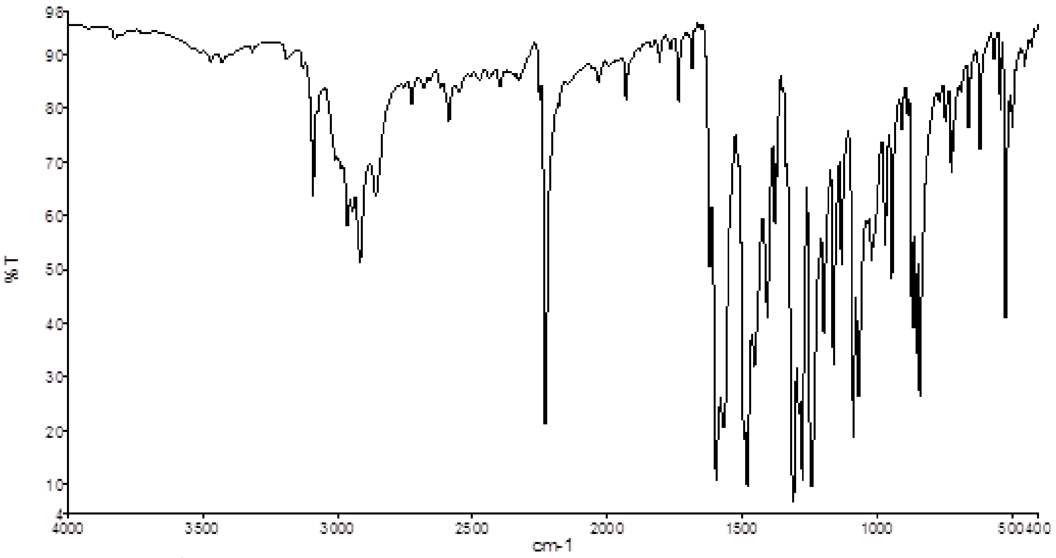


Figure 7. The FT-IR spectrum of compound (**3**).

The vibrational spectra of the compound (**3**) has some characteristic bands of the stretching vibrations such as C-H, C≡N, C=C, and C-O. The C-H are recorded at 3091.44-2860.18 cm^{-1} in the FT-IR spectrum, 3117.05-2927.15 cm^{-1} in the theoretical IR spectrum of the compound (**3**) as a result of characteristic feature C-H stretching bands are assigned at 3100-3000 cm^{-1} region in aromatic groups, at 3000-2700 cm^{-1} in aliphatic groups [45]. The asymmetric and symmetric C-H stretching vibrations modes were recorded at 3039.62-2970.46 cm^{-1} and

2931.38-2927.15 cm^{-1}, respectively. These assignments are compatible with the knowledge which defines C-H asymmetric and symmetric stretching vibrations for methyl groups occur at 3091.44 and 2860.18-2964.81 cm^{-1} [46]. In the other studies, strong C≡N stretching band, characteristic of the vibrations of phthalonitrile moiety, is observed 2234.13, 2258.71 cm^{-1} for 6-31G(d) [41], 2234.65, 2260.14 cm^{-1} for 6-31G(d) [47], 2923-2243 cm^{-1}, 2928-2264 cm^{-1} for 6-31G(d) [43] while this band is recorded at 2230.76 and 2264.60 cm^{-1} in this study, as experimental and computed values, respectively. This mode was observed about 2232-2237 cm^{-1} and 2230 cm^{-1} as experimentally in phthalonitrile groups [48, 49]. The C=C stretching modes belong to aromatic groups are appeared at 1400-1600 cm^{-1} bandwidth, and in accordance with this information these modes are recorded 1597.30, 1605.78 cm^{-1} in trimethylbenzene and 1566.41, 1584.88, experimentally and theoretically, respectively, for the compound (**3**). The C_{Ar}-O stretching vibration mode of the ether group is observed at 1311.58, 1278 cm^{-1} as experimental and as theoretical 1227.18 cm^{-1}, so these values are agreement with the literature that recorded about 1300-1000 cm^{-1} [50]. Some of the C-H in-plane and out-of plane bending vibrations bands and the deformation modes on the functional groups are shown in Table 3.

The selected vibrational frequencies have a good correlation with corresponding spectral values and similar studies in literature. And the correlation graphic (R^2 value is 0.9987) is shown in Figure 8.

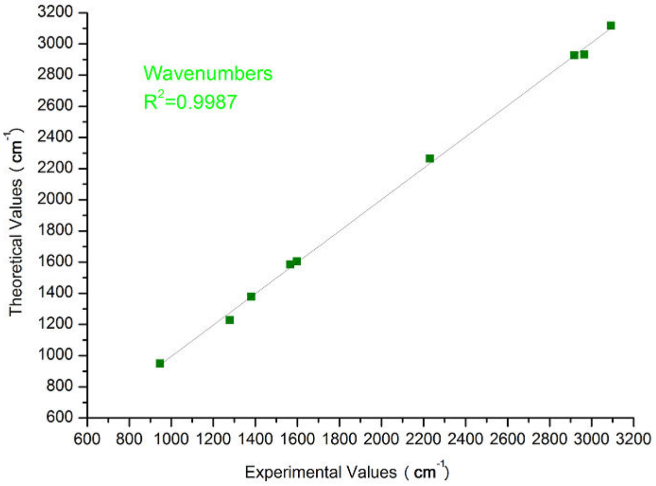


Figure 8. The correlation plot for experimental and theoretical wavenumbers of the compound (**3**).

Table 3. The comparison of the observed and calculated vibrational spectra of the compound (**3**).

Assignments	*Experimental FT-IR (cm^{-1}) with KBr*	*Calculated (cm^{-1}) DFT/B3LYP/6-311G(d,p)*
ν_sC–H$_{(phthalonitrile)}$	3091.44	3117.05
ν_{as}C–H$_{(phthalonitrile)}$	-	3093.85
ν_sC–H$_{(trimethylbenzene)}$	-	3076.86
ν_{as}C–H$_{3(trimethylbenzene)}$	-	3039.62-2970.46
ν_sC–H$_{3(trimethylbenzene)}$	2964.81-2917.12	2931.38-2927.15
νC≡N	2230.76	2264.60
νC=C$_{(trimethylbenzene)}$	1597.30	1605.78
νC=C$_{(phthalonitrile)}$	1566.41	1584.88
νC–C$_{(phthalonitrile)}$	-	1543.31
γ*C-H*$_{(phthalonitrile)}$	-	1471.73
ωC–H$_{3(trimethylbenzene)}$	1380.52	1378.05
νC–O	1278	1227.18
δC–H$_{(phthalonitrile)}$	946.20	949.40
$\theta_{(phthalonitrile)}$	-	715.40
βccc	-	561.89

Vibrational modes: ν; stretching (s; symmetric, as; asymmetric), γ; rocking, ω; wagging, δ; twisting, β; deformation in-plane, θ; ring breathing.

NMR Spectral Analysis

Spectral and theoretical ^{13}C-NMR and ^{1}H-NMR chemical shift values of the compound (**3**) were recorded within the range of 162.05-11.82 ppm, 171.80-13.69 ppm and 7.69-2.00 ppm, 7.94-1.86 ppm respectively, and results are shown in Table 4.

Table 4. Experimental and theoretical ^{13}C NMR and ^{1}H NMR isotropic chemical shift values for the compound (**3**).

Atom	***Experimental chemical shift values (ppm)***	***Theoretical chemical shift values (ppm)***
C1	117.60	121.86
C2	108.14	113.66
C3	135.35	143.85
C4	120.52	129.19
C5	162.05	171.80
C6	120.64	125.20
C7	115.08	123.95
C8	115.49	121.50
C9	151.18	158.70
C10	118.92	125.25
C11	139.54	149.28
C12	128.91	135.14
C13	134.24	145.93
C14	125.55	135.45
C15	19.96	23.59
C16	20.83	23.32
C17	11.82	13.69
H3	7.69	7.94
H4	7.17	7.70
H6	7.15	6.69
H10	6.64	6.82
H12	6.95	7.38
H15[a]	2.30	2.35
H16[a]	2.30	2.36
H17[a]	2.00	2.11

Note: The atom numbering according to Fig.5 used in the assignment of chemical shifts. [a] *Average*

As it can be seen in Table 4, C5 atom has the highest chemical shift values in the downfield observed at 162.05 ppm, 171.80 ppm for as experimental, theoretical, respectively. Another the highest chemical shift value is stated as 151.18 and 158.70 ppm for C9 atom. It has less chemical shift value than C5 atom by reason of the effect of electron withdrawing substituent.

The aromatic carbon atoms have chemical shift values special to aromatic ring carbon atoms (100-150 ppm) [51] and these were recorded 108.14-115.08 ppm experimentally, 113.66-123.95 ppm theoretically for phthalonitrile ring atoms, 118.92-134.24 ppm for experimentally, and 125.25-145.93 for theoretically calculated benzene ring atoms. C1 and C8 atoms have typical triple bond with nitrogen chemical shift values, and were observed 117.60-115.49 ppm and 121.86-121.50 ppm as experimental and theoretical. sp^3 hybridized C15, C16, C17 atoms of the methyl groups have low chemical shift values in the upfield, these values confirm that information sp^3 hybridized methyl group protons are assigned at 0-30 ppm [50].

The chemical shift values belong to aromatic hydrogen atoms-H3, H4, H6, H10 and H12 atoms- are 7.69-6.95 ppm as spectral values, 7.94 and 6.82 ppm as computed values GIAO method. These resonance values are in concert with the literature [43, 52] that indicates as 6.0-8.5 ppm for aromatic protons. And the chemical shift values of the methyl protons, H15, H16 and H17, are assigned 2.30, 2.00 ppm as experimental and 2.35, 2.36, 2.11 ppm average values as theoretical.

Both spectral and theoretical chemical shift values are in agreement with literature values and with each other. The experimental ^{13}C-NMR and ^{1}H-NMR spectra are shown in Figure 9. To compare the experimental and theoretical values, the correlation coefficients and graphics were examined, R^2 value is 0.9992 for ^{13}C-NMR, 0.9849 for ^{1}H-NMR, and they are shown in Figure 10.

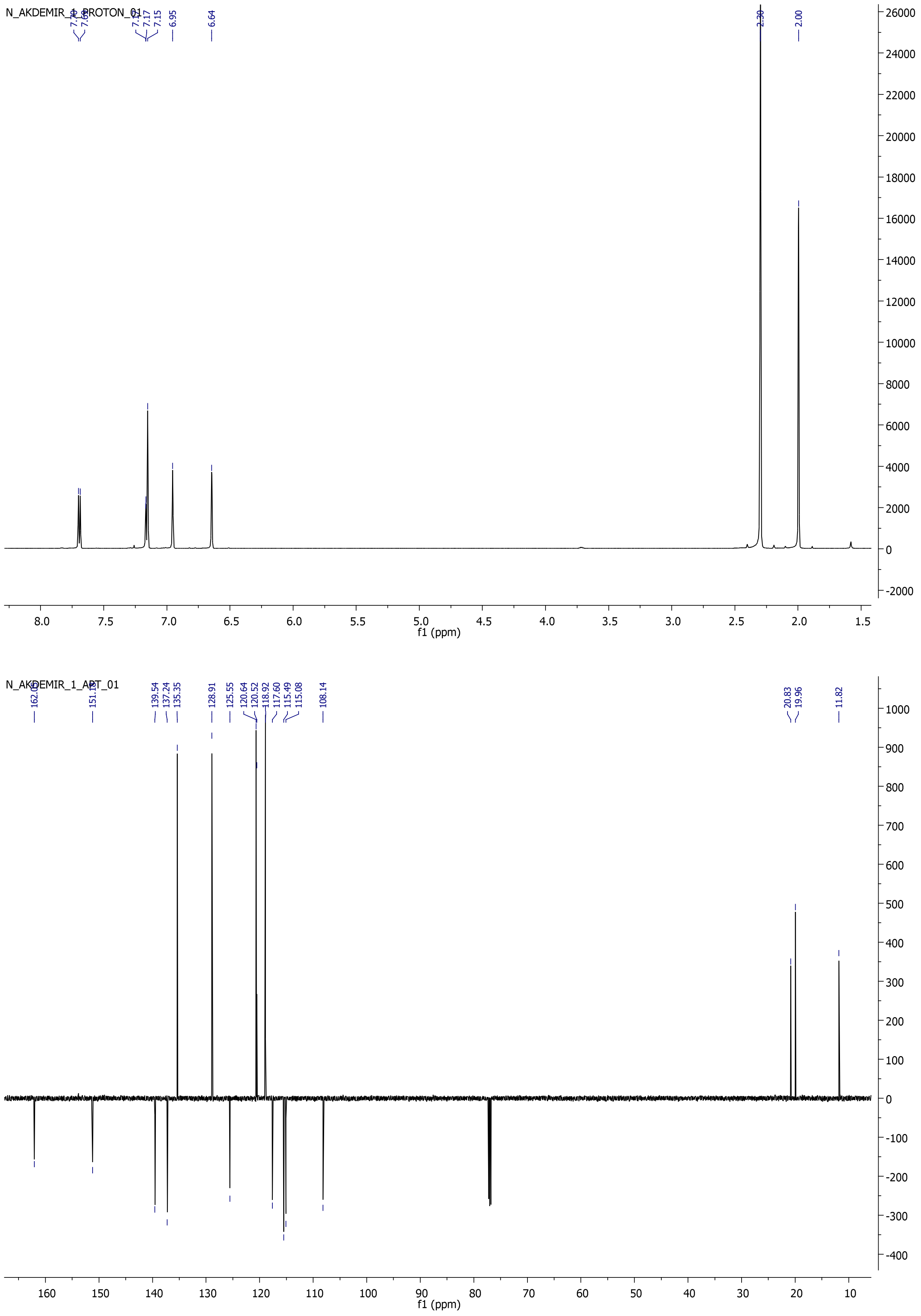


Figure 9. Top)^{1}H NMR spectrum**, bottom)**^{13}C NMR spectrum (APT) of compound (**3**)

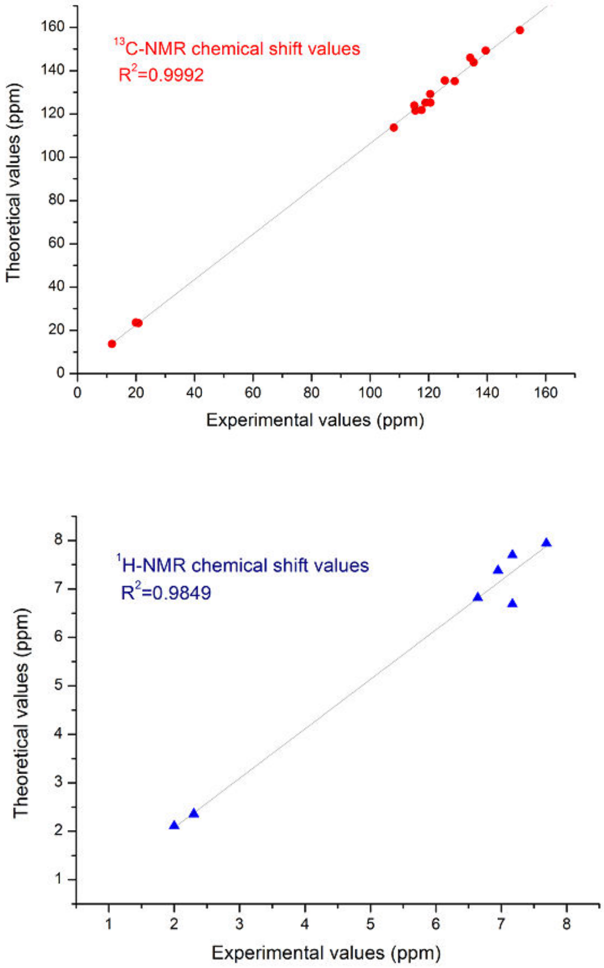


Figure 10. Correlation graphics between the experimental and theoretical Top) ^{13}C-NMR, bottom)^{1}H-NMR chemical shift values of the compound (**3**).

CONCLUSION

Cu(II) and Co(II) phthalocyanines containing 2,3,5-trimethylphenoxy on the periphery were successfully prepared. Structures of all synthesized compounds were determined by elemental analyses, UV-Vis, ^{1}H-NMR, ^{13}C-NMR, Mass spectra, and FT-IR spectroscopy. The phthalocyanines showed excellent solubility in general organic solvents such as DCM, THF, chloroform, DMF, DMSO, and toluene. The absorption spectra of the new phthalocyanines were recorded in different solvents. The aggregation behaviors of compound (**4**) and (**5**) were investigated at different concentrations in THF. Also, computational studies on compound (**3**) were performed with DFT/B3LY/6-311G(d,p) basis set over the ground state and gas phase. So as to support that, the results of experimental were compared molecular structure parameters, vibrational frequencies, ^{1}H-NMR and ^{13}C-NMR chemical shift values. In comparison experimental with theoretical values, it is seen that most of the parameters are slightly different, as experimental results over the solid state, theoretical ones over the gas phase. And, correlation coefficients which were obtained indicate in compliance with results of both spectral and modelling that is not only among themselves but also other phthalonitrile studies. The author hopes that these consequences will be created an infrastructure for researchers carrying out similar studies and can be used for the further analysis.

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Türkçe Öz ve Anahtar Kelimeler

Yeni, Periferal Konumlarda 2,3,5-Trimetilfenoksi Sübstitüe Cu ve Co Ftalosiyaninlerin Sentezi, Karakterizasyonu ve Spektroskopik Özelliklerinin İncelenmesi, 4-(2,3,5-trimetilfenoksi)ftalonitrilin Hesaplamalı ve Deneysel Çalışmaları

Nesuhi Akdemir[1]

Öz: 4-(2,3,5-trimetilfenoksi)ftalonitril (**3**) nükleofilik aromatik sübstitüsyon ile hazırlanmış ve FT-IR, kütle spektrometrisi, ^{1}H ve ^{13}C-NMR teknikleriyle karakterize edilmiştir. **3** bileşiğinin moleküler yapısı Yoğunluk Fonksiyonel Teorisi (DFT/B3LYP) yöntemiyle temel halde 6-311G(d,p) taban seti ile en uygun hale getirilmiştir. X-ışını tek kristal saçılması yöntemiyle moleküler geometrik parametreler elde edilmiştir, spektral sonuçlar hesaplanan bağ uzunlukları ve açıları, titreşim frekansları ve ^{1}H ile ^{13}C kimyasal kaymaları ile karşılaştırılmıştır. Bunun dışında, dinitril türevinin susuz $CuCl_2$ veya $CoCl_2$ ile azot atmosferinde kuru n-pentanol içinde 140 °C'de tepkimeye sokulmasıyla karşılık gelen Cu(II) ve Co(II) ftalosiyaninler elde edilmiştir. Yeni bileşikler elementel analiz, FT-IR ve elektronik soğurma spektrumu ile belirlenmiştir. Cu(II) ve Co(II) ftalosiyaninlerin UV-Vis spektrumları THF içinde farklı derişimlerde kaydedilmiş ve ayrıca başka çözücüler de (DMF, DMSO, DCM, $CHCl_3$ ve toluen) denenmiştir.

Anahtar kelimeler: Ftalosiyaninler; ftalonitril; 2,3,5-trimetilfenol; DFT.

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