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# The Oxidation of 4-(4-Formylphenoxy) Phthalonitrile to 4-(4-Carboxylphenoxy) Phthalonitrile at Ambient Conditions

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**Abstract.** The substituted phthalonitriles have been used to prepare soluble phthalocyanine species in recent years. One of the most used phthalonitrile derivatives for the target product is 4-nitrophthalonitrile. In this study 4-(4-formylphenoxy) phthalonitrile was prepared as the substituted phthalonitrile derivative by the nucleophilic substitution reaction of para-hydroxybenzaldehyde with 4-nitrophthalonitrile. During the crystallization of the product by slow evaporation technique, it readily self-oxidized to 4-(4-carboxylphenoxy) phthalonitrile at ambient condition open to air. The crystal structure of the molecule was determined by XRD technique. The molecule crystalizes at triclinic space group P-1 and the unit cell parameters of crystal are $a$=6.3591 (10) Å, $b$=7.5464 (11) Å, $c$=13.819 (2) Å, $\alpha$=88.434 (11)°, $\beta$=87.942 (12)°, $\gamma$=80.111 (12)° and $Z$=2. The crystal structure has intermolecular O—H···O, C—H···N and C—H···O hydrogen bonds. In addition to these hydrogen bonds, C—N···Cg and Cg···Cg interactions are present between molecules. In the crystal, intermolecular O—H···O hydrogen bonds occur between molecular units in a dimeric molecular form. Molecular structure, vibrational frequencies and $^{1}$H and $^{13}$C NMR chemical shifts of the target compound have been calculated by using B3LYP method with 6-311++G(d, p) basis set, as well.

***Keywords*:** Substituted phthalonitrile, Crystal structure, Oxidation, Theoretical calculation.

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# 4- (4-formilfenoksi) ftalonitrilin 4- (4-karboksilfenoksi) ftalonitril'e Ortam Koşullarında Oksidasyonu

**Özet.** Sübstitüe ftalonitriller, son yıllarda çözünür ftalosiyanin türlerini hazırlamak için kullanılmaktadır. Hedef ürün için en çok kullanılan ftalonitril türevlerinden biri, 4-nitroftalonitrildir. Bu çalışmada, 4-(4-formilfenoksi) ftalonitril, para-hidroksibenzaldehidin 4-nitroftalonitril ile nükleofilik yerdeğiştirme reaksiyonu ile sübstitüe ftalonitril türevi olarak hazırlanmıştır. Ürün yavaş buharlaştırma tekniği ile kristallendirilmesi sırasında, havaya açık ortam koşullarında, 4- (4-karboksilfenoksi) ftalonitril'e kendiliğinden oksitlenmiştir. Molekülün kristal yapısı XRD tekniği ile belirlendi. Molekül, triklinik uzay grubu P-1'de kristallenmiştir ve kristalin birim hücre parametreleri a = 6.3591 (10) Å, b = 7.5464 (11) Å, c = 13.819 (2) Å, a = 88.434 (11) °, 87 = 87.942 (12) °, $\gamma$ = 80.111 (12) ° ve Z = 2’ dir. Kristal yapı moleküllerarası O — H ··· O, C — H ··· N ve C — H ··· O hidrojen bağlarına sahiptir. Bu hidrojen bağlarına ek olarak, moleküller arasında C — N ··· Cg ve Cg ··· Cg etkileşimleri mevcuttur. Kristalde moleküllerarası O — H ··· O hidrojen bağları, bir dimerik yapı içinde moleküler birimler arasında meydana gelir. Hedef bileşiğin, moleküler yapısı, titreşim frekansları ve $^{1}$H ve $^{13}$C NMR kimyasal kaymaları da 6-311 ++ G (d, p) temel seti ile B3LYP metodu kullanılarak hesaplanmıştır.

***Anahtar Kelimeler*:** Sübstitüe ftalonitril, Kristal yapı, oksidasyon, teorik hesaplama.

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## 1. INTRODUCTION

Phthalonitriles are known a starting material in the synthesis of symmetrically and unsymmetrically phthalocyanines [1]. Substituted phthalonitriles are the most important phthalocyanine precursors due to the substituent effect on the phthalocyanine properties. Synthesis of phthalonitriles carrying functional groups leads to functionalized phthalocyanines which are of great importance for the targeted applications such as catalysis [2], liquid crystals [3], photosensitizers for PDT [4], non-linear optics [5], nanotechnology [6] and dye-sensitized solar cell [7]. Tetra-substituted phthalocyanines are generally obtained from mono-substituted phthalonitriles [8].

Phthalocyanines (Pcs) carrying purposive groups such as carboxyl, amines and hydroxyl groups are attractive target for chemists due to phthalocyanine-based multicomponent systems as new molecular materials [9-12].

Schif bases are one of the parts of used chelate compounds for the advancement of coordination chemistry since it could generate complexes with most transitions metals. The imine formation *via* aldehyde groups is a complementary system with excellent building block potential for further applications. It is very important to produce Pcs containing the aldehyde group from the corresponding phthalonitrile since they may carry out further chemical reactions on the macrocycle rings to prepare Schiff's base metal complex substituted phthalocyanines. Therefore, we have recently described a model study; the synthesis, characterization and fluorescence properties of two salicyhydrazon Zn complexes substituted zinc-phthalocyanine as a new functionalized material. It was obtained the reaction of the metal salt with imine group achieved from aldehyde group on Pc [13].

In this study, we have presented the self-oxidation of 4-(4-formylphenoxy) phthalonitrile to 4-(4-carboxylphenoxy) phthalonitrile which was observed during the experimental procedure. The synthesis and characterization of 4-(4-formylphenoxy) phthalonitrile have been performed to prepare an alternative starting material for the synthesis of different aldehyde substituted phthalocyanines. During the crystallization process of the aldehyde substituted phenoxy phthalonitrile prepared as the starting material, it was determined that the target product self-oxidized to the acid form by air oxygen at ambient condition. So the obtained results were decided to present. The structural crystallographic characterization of oxidized form is studied. The theoretical calculations were also performed for both the aldehyde and acidic forms.

## 2. EXPERIMENTAL AND THEORETICAL PROCEDURE

### 2.1. Materials and measurements

4-Hydroxybenzaldehyde, deutorated chloroform, dimethylformamide (DMF), dichloromethane (DCM), hexane and chloroform were obtained from Sigma-Aldrich. The drying and cleaning of all solvents were performed as determined by Perrin and Armarego [14]. The reported literature was followed for the preparation of 4-nitrophthalonitrile [15]. Thin-Layer chromatography (TLC) containing silica gel 60 $HF_{254}$ as an adsorbent was used to check the progress of the reaction. Column chromatography with silica gel (Merck grade 60) was applied to provide the purification. Melting points (m.p.) were found out with the Barnstad-Electrotermel 9200. Infrared spectra were obtained by using Perkin Elmer Spectrum two FT-IR spectrophotometer existed with Perkin Elmer UATR-TWO diamond ATR. $^{1}$H ve $^{13}$C NMR spectra were gained with Varian Mercury Plus 300 MHz spectrometer.

### 2.2. Computational Details

The ground state geometry of 4-(4-formylphenoxy)phthalonitrile was taken into account by using density functional theory (DFT) with B3LYP (Becke's three-parameter hybrid functional using the LYP correlation functional) at 6-311++G(d,p) level [16,17]. In this work, Gaussian 09W program package [17] and Gauss-View molecular visualization program [18] were used to find out the optimized geometry of the structure, IR spectra, $^{1}$H and $^{13}$C NMR chemical shifts of 4-(4-formylphenoxy) phthalonitrile. Furthermore, the theoretical harmonic vibrations of the molecule were scaled by 0.9608 and these frequencies were compared with the experimental results.

## 2.3. Synthesis

### 2.3.1. 4-(4-formylphenoxy)phthalonitrile, 1

The expected compound (**1**) was obtained as a cream colored powder according to published procedure [19]. The purification of the compound was achieved with the column chromatography on silica-gel by using chloroform as mobile phase. Yield 1.3 g, 90.0 %. m.p: 154 °C. FT-IR (PIKE MIRacle$^{TM}$ ATR) ν max/cm$^{-1}$: 3104-3043 (Ar,C-H), 2858, 2746 (Aldehyde C-H), 2238 (C≡N), 1691 (C=O), 1606-1502 (Ar, C=C), 1489-1309 (Ar C-C), 1255 (Ar-O-Ar), 1209, 1155, 1111, 1087, 950, 858, 839, 821. $^1$H-NMR (CDCl$_3$) δ (ppm) : 10.03 (s, 1H), 8.01 (d, 2H), 7.81 (d, 1H), 7.40 (d, 1H), 7.35(d, 1H), 7.23 (d, 2H). $^{13}$C-NMR (CDCl$_3$) δ (ppm): 190.68, 160.34, 159.10, 135.94, 134.09, 132.64, 123.03, 122.89, 120.59, 118.21, 115.32, 114.90, 110.56.

### 2.3.2. 4-(4-carboxylphenoxy)phthalonitrile, 2

4-(4-formylphenoxy)phthalonitrile (1) was attempted to crystallize in chloroform by slow evaporation technique to obtain single-crystal. Single-crystal X-ray studies showed that during the crystallization of this compound, it oxidized to 4-(4-carboxylphenoxy) phthalonitrile by exposing the air oxygen at ambient condition. FT-IR (PIKE MIRacleTM ATR) □ max/cm-1: 3400-2552 (O-H), 3087-3039 (Ar,C-H), 2231 (C≡N), 1673 (C=O), 1603-1503 (Ar, C=C), 1487-1421 (Ar C-C), 1250 (Ar-O-Ar), 1210, 951, 845.1H-NMR (CDCl3) δ (ppm): 8.15 (d, 1H), 8.02 (d, 1H), 7.93 (s, 1H), 7.54 (d 1H), 7.25 (d, 2H).13C-NMR (CDCl3) δ (ppm): 224.16, 167.25, 162.14, 134.42, 130.13, 123.54, 122.53, 120.50, 117.27, 115.78, 114.58, 113.82, 108.27.

## 2.4. X-Ray Crystal Structure Determination

Single crystal X-ray data were picked up with a Stoe IPDS II [20] single crystal diffractometer at 296 K and were used monochromated MoK$_\alpha$ radiation. Cell refinement and data reduction were performed with X-AREA [20] and X-RED [20] programs. It was used SHELXS-97 [21] program to solve structure and SHELXL-97 [21] program to refine structure. ORTEP-3 for Windows [22] to obtain figures, WinGX [23] and PLATON [24] software to prepare material for publication were used.

All hydrogen atoms were positioned geometrically (C-H=0.930 Å, O-H=0.820 Å) and treated as riding with $U_{iso}$(H)=1.2$U_{eq}$(C), $U_{iso}$(H)=1.5$U_{eq}$(O). The crystal data and refinement of the compound **2** are shown in Table 1.

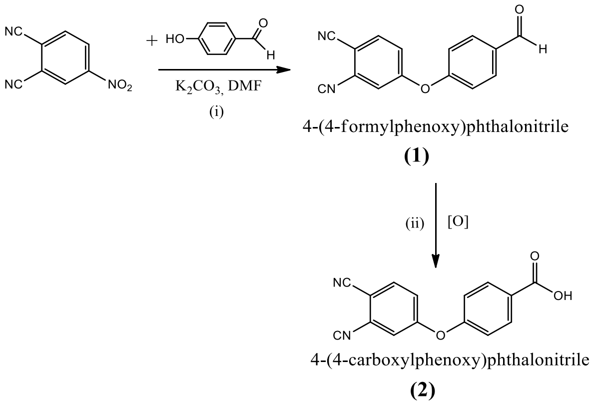
**Table 1.** Crystal data and structure refinements of the title compound

| | |
|---|---|
| **Formula** | $C_{15}H_8N_2O_3$ |
| **Crystal System** | Triclinic |
| **Color / Shape** | Colorless / Plate |
| **Crystal size** | 0.64×0.29×0.05 mm |
| **Temperature** | 296 K |
| **Space Group** | P-1 |
| **Unit Cell Dimensions** | |
| ***a*** | 6.3591 (10) Å |
| ***b*** | 7.5464 (11) Å |
| ***c*** | 13.819 (2)Å |
| ***α*** | 88.434 (11)° |
| ***β*** | 87.942 (12)° |
| ***γ*** | 80.111 (12)° |
| **h / k / l** | -7, 7 / -9, 9 / -17, 17 |
| **Volume** | 652.70 (17) Å$^3$ |
| ***Z*** | 2 |
| **Density (calculated)** | 1.344 mg/m$^3$ |
| **Radiation** | MoKα (λ=0.71073 Å) |
| **Absorption coefficient (*μ*)** | 0.10 mm$^{-1}$ |
| **Absorption correction** | Integration X-RED |
| ***F*(000)** | 272 |
| **θ Ranges** | 2.7° / 26.5° |
| **Observed reflections, I>2σ(I)** | 721 |
| **Independent Reflections** | 1460 (Rint=0.100) |
| **Measured Reflections** | 5818 |
| **Data / Restrains / Parameters** | 1463 / 0 / 182 |
| **Maximum shift / error** | 0.00 |
| **S** | 1.04 |
| **Final R indices [I>2σ(I)]** | R1=0.055, *w*R($F^2$)=0.111 |
| **Largest diff. Peak and hole** | 0.09 eÅ$^{-3}$, -0.11 eÅ$^{-3}$ |

## 3. RESULT AND DISCUSSION

### 3.1. Synthesis and Spectroscopic Characterization

The synthetic pathway to obtain 4-(4-carboxylphenoxy) phthalonitrile can be presented as seen in Scheme 1.



**Scheme 1.** *Reagent and conditions*: (i). 4-hydroxybenzaldehyde, DMF, $K_2CO_3$, (90%); (ii) in air at room temperature

The 4-(4-formylphenoxy)phthalonitrile (**1**) was obtained as powder from the reaction of 4-hydroxybenzaldehyde and 4-nitrophthalonitrile in presence of $K_2CO_3$ in DMF by keeping on stirring at ambient temperature for 24h. 4-(4-carboxylphenoxy)phthalonitrile (**2**) was obtained with the oxidation of 4-(4-formylphenoxy) phthalonitrile at ambient condition by air during the slow evaporation crystallization process of compound **1**.

The verification of the obtained products was provided by spectroscopic methods including $^1$H NMR, $^{13}$C NMR, FT-IR, and melting point. All spectral data confirm the proposed structures.

When the results of **1** to p-hydroxybenzaldehyde are compared, the replacement of the –OH peak with new bands at 1691 cm$^{-1}$, 1255 cm$^{-1}$, and 2237 cm$^{-1}$, belonging to the -C=O, Ar-O-Ar and -C≡N vibrations respectively clearly indicate the formation of **1**. The aldehyde C-H vibrations were detected as the Fermi resonance in between 2858 cm$^{-1}$ and 2746 cm$^{1}$ at the FT-IR spectrum of **1,** supporting this event, as well.

In the FT-IR spectrum of **2**, the oxidation of **1** was confirmed by the shifting of C=O stretching vibration from 1691 cm$^{-1}$ to 1673 cm$^{-1}$ due to resonance of carboxyl group with the phenyl ring and the C=O band was calculated at: 1746 cm$^{-1}$ using B3LYP method with 6-311++G(d, p) basis set. The O-H vibration appeared at 3400-2552 cm$^{-1}$ as the broad and distorted typical organic acid vibrations due to the strong inter and intramolecular hydrogen bond formation, and the O-H vibration bands were calculated at; 3662 cm$^{-1}$ using B3LYP method with 6-311++G(d, p) basis set. Furthermore, the disappearances of bands at 2858-2746 cm$^{-1}$ region, which are arised from the Fermi resonance, confirm the conversion of the aldehyde group, as well. The shifting of the significant C≡N vibration of **1** at 2239 cm$^{-1}$ to 2231 cm$^{-1}$ for **2** supports the proposed conversion as shown in Fig. 1. The aromatic C-H vibrations of both molecules are also appeared at different wavelengths at 3104-3043 cm$^{-1}$ for **1** and at 3087-3039 cm$^{-1}$ for **2,** as expected. The C-H vibration bands were calculated at; 3216-3195 cm$^{-1}$ for **2** using B3LYP method with 6-311++G(d, p) basis set.

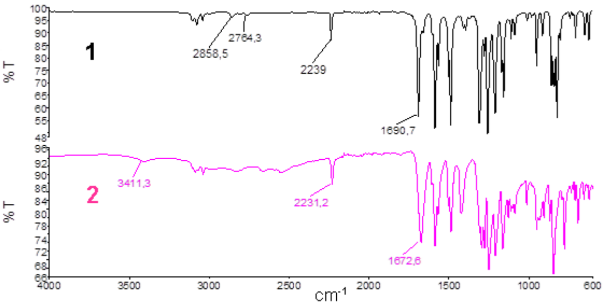


**Figure 1.** FT-IR spectra of **1** and **2**

The $^1$H NMR and $^{13}$C NMR data gave satisfactory information about the obtained molecules *via* the proposed conversions. In the $^1$H NMR spectra of **1**, the disappearances of OH peak of p-hydroxybenzaldehyde and the appearance of new peaks in aromatic region (8.01-7.23 ppm) are the proof for the formation of **1.** The aldehyde proton signal was predicted as 10.03 ppm which was different from the starting material. Also in this study, the aldehyde proton signal and the aromatic region were calculated as 10.05 ppm and 7.77-

7.01 ppm respectively at the $^{1}$H NMR spectrum of **1** using B3LYP method with 6-311++G(d, p) basis set. In the $^{13}$C NMR spectrum of **1** the appearance of the signal at 115.32 and 114.90 ppm (that calculated at; 119.02 and118.74 ppm using DFT) belonging to the nitrile carbon atom is the clearly different from p-hydroxy benzaldehyde.

In the $^{1}$H NMR spectra of **2**, the expected O-H proton of carboxylic acid group was not observed in the region. It has shifted strongly to the upper field and disappeared which was the evidence of the strong hydrogen bond formation between the acid molecules which caused to dimeric molecular form determined by the crystallographic studies. The other signals belonging to the acid form (**2**) were determined in the aromatic region which was totally different from the aldehyde form (**1**). In the $^{13}$C NMR spectra of **2**, the expected carbon signal of carboxylic acid group was observed at 224.16 ppm which differs from compound **1**.

In this study, the total energy of the molecules (**1**) and (**2**) were calculated as -836.54 and -911.80 a.u. respectively using B3LYP method with 6-311++G(d, p) basis set. According to the above results it can be said that molecule **2** is more stable from molecule **1** which obviously illustrates why the aldehyde form of the prepared molecules (**1**) easily self-oxidize the acid form (**2**) by air oxygen during the crystallization process.

### 3.2. Synthesis and Spectroscopic Characterization

The asymmetric unit of the title compound is given in the Fig. 2. The molecule has two cyano groups and the triple C—N bond distances belong to these groups are 1.138 (6) Å for C1—N2 and .147 (6) Å for C8—N1.These bond distances were calculated 1.155 Å for C1—N2 and 1.154 Å for C8—N1. These triple C—N bond distances agree with the literature [25, 26]. The N2—C1—C2 and N1—C8—C7 bond angles are 178.7 (6)˚ and 179.0 (5)˚ and these angles were calculated at; 178.4˚ and 178.3˚ respectively. These bond angles deviate a small amount from linearity, because of the intermolecular hydrogen bonds. The C—C aromatic bond distances range from 1.411 (5) Å to 1.368 (6) Å. Two aromatic rings are present in the molecule and these rings are almost planar (r.m.s. deviations are 0.0061 Å for C2/C7, 0.0035 Å for C9/C14) and dihedral angle between these rings is 67.19 (15)°. The aromatic rings are linked *via* oxygen atom and C5**—**O3**—**C11 bond angle is 119.3 (4)°. Some selected bond distances, bond angles and torsion angles are given in Table 2.

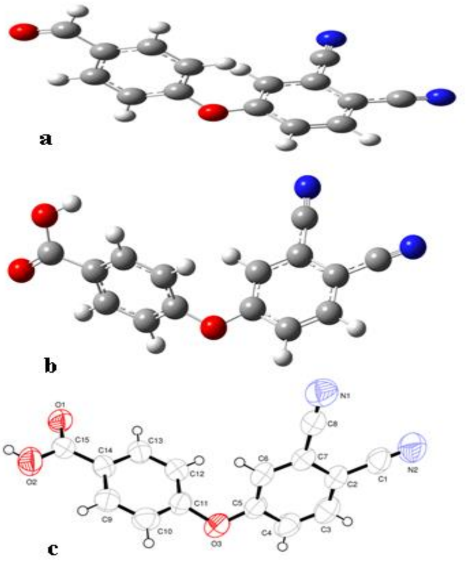


**Figure 2.** (a) Optimized molecular structure (with B3LYP/6-311++G(d,p) level) of acid form (**2**), (b) Optimized molecular structure (with B3LYP/6-311++G(d,p) level) of aldehyde form (**1**), (c) The experimental geometric structure of the title compound.

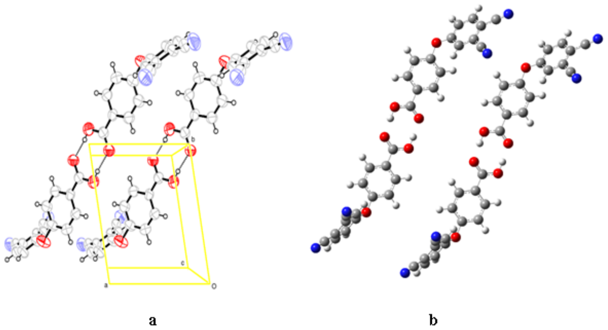


**Figure 3.** (a) Experimental and (b) theoretical dimer structure of the title compound

**Table 2.** Some selected bond distances, bond angles and torsion angles of the title compound (Å, °)

| Atoms | Experimental | B3LYP | Atoms | Experimental | B3LYP |
|---|---|---|---|---|---|
| C1—N2 | 1.138 (6) | 1.155 | C8—N1 | 1.147 (6) | 1.154 |
| O1—C15 | 1.249 (5) | 1.200 | O2—C15 | 1.299 (5) | 1.359 |
| O3—C5 | 1.373 (5) | 1.367 | O3—C11 | 1.398 (6) | 1.387 |
| N1—C8—C7 | 179.0 (5) | 178.3 | N2—C1—C2 | 178.7 (6) | 178.4 |
| O1—C15—O2 | 121.0 (5) | 119.9 | C5—O3—C11 | 119.3 (4) | 121.2 |
| O1—C15—C14 | 122.5 (5) | 123.1 | | | |
| C6—C7—C8—N1 | −107 (31) | 105.651 | N2—C1—C2—C3 | 41 (24) | 42.295 |
| C13—C14—C15—O1 | 4.0 (7) | 4.101 | | | |

**Table 3.** Hydrogen-bond geometry (Å,°)

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2···O1$^{i}$ | 0.82 | 1.82 | 2.632 (5) | 171 |
| C3—H3···N2$^{ii}$ | 0.93 | 2.55 | 3.477 (6) | 178 |
| C4—H4···O1$^{iii}$ | 0.93 | 2.57 | 3.475 (6) | 163 |
| C6—H6···N1$^{iv}$ | 0.93 | 2.53 | 3.450 (5) | 170 |

**Symmetry codes:** (i) $-x, -y+2, -z$; (ii) $-x+3, -y, -z+1$; (iii) $x+1, y-1, z$; (iv) $-x+1, -y+1, -z+1$.

The crystal structure has intermolecular O—H···O, C—H···N and C—H···O hydrogen bonds. While the carboxyl groups of the molecules establish $R_2^2(8)$ dimers *via* intermolecular O—H···O hydrogen bonds belong to graph set notation in the crystal structure, the cyano groups of the molecules create $R_2^2(10)$ motifs *via* intermolecular C—H···N hydrogen bonds. The C—H···N hydrogen bonds create a hydrogen-bonded chain running parallel to the [-110] direction. The geometric parameters of O—H···O hydrogen bond are 0.82 Å, 1.82 Å, 2.632 (5) Å and 171°. The O—H···O hydrogen bond are calculated at; 1.014 Å, 1.608 Å, 2.622 Å and 1.039 Å, 1.608 Å, 2.2.647 Å, respectively, using B3LYP-6-311++G(d, p) basis level as seen Fig. 3. In addition to these hydrogen bonds, C—N···Cg and Cg···Cg interactions are present in the crystal structure. The geometric parameters of hydrogen bonds are given in Table 3.

## 4. CONCLUSION

We have reported the synthesis of 4-(4-formylphenoxy)phthalonitrile (**1**) as an aldehyde-substituted phthalonitrile playing a key component in the chemistry of phthalocyanine. It is crucial to obtain phthalocyanines containing reactive functional groups in this way in order to be able to further chemical reactions on Pc macrocycles. During the crystallization process of the compound (**1**), we observed that aldehyde groups oxidized easily to carboxyl group even with air $O_2$. The new carboxyl phthalonitrile derivative obtained by self-oxidation of aldehyde group has been characterized by FT-IR, $^1$H-NMR, $^{13}$C-NMR. The crystal structure of the molecule (**2**) was determined by XRD technique and also, theoretical calculations were performed. X-ray diffraction data show that the crystal structure has O—H···O, C—H···N, C—H···O hydrogen bonds. In addition to these hydrogen bonds, the crystal structure has also C—N···Cg and Cg···Cg interactions. Hydrogen bonds together with these interactions are effective in crystal packaging. The molecule (**2**) is more stable than compound (**1**) with respect to the calculated total energies of the molecules. Furthermore, all crystallographic data agree with the theoretical bond lengths, angles, dihedral angles of the compound **2**.

## APPENDIX A. SUPPLEMENTARY DATA

CCDC 1041091 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge *via* https://www.ccdc.cam.ac.uk/services/structure_deposit/, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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