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Synthesis, crystal structure and electronic applications of monocarboxylic acid substituted phthalonitrile derivatives combined with DFT studies



Gülenay Tunç^a, Betül Canımkurbey^{b,c}, Burcu Dedeoğlu^a, Yunus Zorlu^a, Serpil Eryılmaz^{d,*}, Ayşe Gül Gürek^{a,*}

^a Gebze Technical University, Department of Chemistry, 41400 Gebze, Kocaeli, Turkey

^b Amasya University, Şerefeddin Health Services Vocational School, 05100 Amasya, Turkey

^c Amasya University, Central Research Laboratory, 05100 Amasya, Turkey

^d Amasya University, Faculty of Arts and Sciences, Department of Physics, 05100 Amasya, Turkey

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ABSTRACT

Monocarboxylic acid substituted phthalonitrile derivatives (PN1 and PN2) have been synthesized and their molecular geometries and hydrogen bond interactions investigated with single cystal X-ray diffraction analysis. PN1-a and PN2 crystal structures linked by a pair of O-H…O hydrogen bonds form classical carboxylic acid inversion dimers, whilst PN1-b crystal structure stabilized by classical O-H-O and O-H…N hydrogen bonding interactions. Spectral characterizations of PN1-a and PN2 structures have been performed by FT-IR, ¹H-¹³C NMR and UV-Vis techniques. Molecular structure optimization and structural properties of PN1 and PN2 in the forms of monomer and dimer have been studied with the DFT approach, B3LYP functional and 6-311++G(d,p) basis set. The effects of dimeric forms of structures on geometrical and spectral parameters have been evaluated together with the values of monomeric forms and experimental ones. Concepts specific to electronic absorption spectra such as absorption wavelengths and major contributions to electronic transitions and FMOs energy values have been determined by TD-DFT approach. Some reactivity properties of the monomer PN1-a and PN2 structures have been evaluated through global, local parameter values and MEP visuals. It was shown that PN2 monomer structure which has both a low HOMO-LUMO energy gap (ΔE =3.83 eV) and a higher chemical softness value (S=0.52 eV^{-1}) is more reactive than **PN1-a** monomer. The potentials of being nonlinear optical (NLO) material and some thermodynamic parameters that are thought to contribute to their structural properties have been determined theoretically for PN1-a and PN2 monomeric forms. Furthermore, it is determined that PN2 has superior properties compared to PN1 based on the electrical characterization of the compounds.

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1. Introduction

Phthalonitriles have attracted attention not only because of being important intermediates or precursors in synthetic chemistry but also due to their potential use in material design for industrial use. Especially they have potential applications in electronics, machinery, automobile, aerospace, and shipping fields for use in military or civilian areas, where high-tech equipment is required [1,2]. Another remarkable application of phthalonitrile derivatives arises from being a candidate material for the development of liquid crystal displays (LCDs) owing to the negative dielectric anisotropy values in their liquid crystalline forms [3-5].

The phthalonitriles play a considerable role as a precursor in the synthesis of phthalocyanine compounds. Phthalocyanine is one of the main compounds of functional macrocyclic organic materials with prominent properties such as similarity with a porphyrin ring structure, high symmetry, planarity of its molecular structure and strong π -electron system [6]. Phthalonitriles may be functionalized with substitution for specific purposes [7,8]. This diversity can pioneer the synthesis of novel phthalocyanine compounds that exhibit different electrical, optical or magnetic properties. It is well known that –COOH group participates in the strong hydrogen bond formation through dimerization between the two carboxylic groups often cyclically bound by a local center of inversion resulting in the formation of diverse complexes governed by the structure and

^{*} Corresponding authors.

E-mail addresses: srpleryilmaz@gmail.com (S. Eryılmaz), gurek@gtu.edu.tr (A.G. Gürek).



Fig. 1. The structure of monocarboxylic acid substituted phthalonitrile derivatives (PN1 and PN2).

strength of the H-bonds with wide applications. Current research has shown that phthalocyanine derivatives containing carboxylic acid (–COOH) as an electron-withdrawing group which will allow charge transfer in the π -conjugated bridging structure are particularly effective in the development of DSSCs [9-11].

Electrical conductivity measurements are important for the determination of organic compounds that have the potential application as electronic materials. Materials having crystal form can be used in electronic device applications due to their high mobility, and they are suitable for organic thin-film device applications by obtaining regular film structures [12].

With the recent advances in computer resources, computation has become an alternative approach to study the nature of many physical and chemical phenomena at the electronic and atomistic level. Quantum chemical methods enable researchers to determine the ground state characteristics of molecular systems, some spectral parameters in the absence of experimental findings and even non-linear optical (NLO) properties.

In this study, we aim to determine the structural properties of two phthalonitrile compounds containing carboxylic acid (-COOH) groups which are considered to have a potential use in optoelectronic applications and to guide the synthesis of new phthalocyanine compounds. Two monocarboxylic acid substituted phthalonitrile derivatives, 3,4-dicyano benzoic acid (PN1) and 4-((3,4-dicyanophenyl)ethynyl)benzoic acid (PN2), were synthesized (Fig. 1). To examine the effect of dimerization on molecular geometry and spectral parameters, theoretical analysis has been carried out by performing Density Functional Theory calculations. Besides, frontier molecular orbitals (FMOs) energies, global and local reactivity descriptors, molecular electrostatic potential (MEP) maps, non-linear optical (NLO) properties and some thermodynamic parameters were examined theoretically for monomers. Investigation of electrical characterization and surface structures, PN1 and PN2 were coated by spin coating method on glass substrates. I-V characteristics of diode were investigated by semiconductor characterization system at room temperature. Surface profiles of PN1 and PN2 films were analysed using Scanning Electron Microscope (SEM).

2. Materials and methods

2.1. General procedure and instruments

Chemicals were purchased from commercial suppliers and used without further purification unless stated otherwise. The monitoring of the reactions was carried out by thin layer chromatography (TLC), employing aluminum sheets coated with silica geltype 60 F254 (0.2 mm thick, E. Merck). Purification and separation of the synthesized products were performed by column chromatography, using silica gel (230–400 mesh, 0.040–0.063 mm, Merck). Eluents and relative proportions of the solvents are indicated for

each case. Column chromatography was carried out on silica gel Merck-60 (230-400 mesh, 60 A), and TLC on aluminum sheets precoated with silica gel 60 F₂₅₄ (E. Merck). Elemental analyses were obtained using a Carlo Erba 1106 Instrument. The infrared spectra were recorded between 4000-650 cm⁻¹ using a Perkin Elmer FT-IR System Spectrum BX with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal. ¹H NMR spectra were recorded on Bruker and Varian INNOVA 500 MHz spectrometers (Fig. S.1 and S.2). Mass spectra of PN2 was performed on a Bruker Daltonics MicrOTOF spectrometer. Positive ion and linear mode MALDI-TOF-MS spectra of the compounds were obtained in 2,5-dihydroxy benzoic acid (DHB) or dithranol (DIT) MALDI matrixes using nitrogen laser accumulating 50 laser shots. Mass spectra of PN1 were obtained using Thermo Scientific- TSQ Fortis mass spectrometer by using ESI technique. Absorption spectra in the UV-Vis region were recorded with a Shimadzu 2600 UV spectrophotometer. I-V characteristics of PN1 and PN2 thin films were investigated by Keithley 4200SCS at room temperature. Surface profiles of PN1 and PN2 films were analyzed using SEM (Philips XL 30 SFEG).

2.2. Synthesis process

Preparation of **3,4-dicyanobenzoic acid** (**PN1**): This compoud is obtained by using three steps reaction pathway.

4-Carboxyphthalimide (1): Ttrimellitic anhydride (10 g, 0.052 mol) was dissolved in 16 ml formamide under argon atmosphere and reflux for 3 hours. After, reaction mixture was cooled to room temperature. After cooling the precipitate was filtered through G3 filter, washed with H₂O and dried at 100 °C in vacuum Yield: 7.75 g (71%), mp: 210°C. FT-IR: ν , cm⁻¹ 3149 (-COH), 3440 (-NH), 1765, 1699 (-C=O), 1621, 1570, 1479, 1455, 1380, 1307, 1264, 1178, 1159, 1096, 1042, 945, 898.

4-carboxyphthalamide (2): Compound 1 (16.8 g, 0.087 mol) was stirred in 32% NH₄OH (113 mL) for 24h at room temperature. The white precipitate of **2** was filtered, washed with H₂O and dried at 100°C in vacuum. Yield: 13 g (76%), mp: 184°C. FT-IR: ν , cm⁻¹ 3448 (-COH), 3316 (-NH₂), 1721 (-C=O), 1456, 1377, 1288, 1248, 1071, 799.

3,4-dicyanobenzoic acid (**PN1**): SOCl₂ (20 ml) was dissolved in dry DMF (46 ml) under argon atmosphere and cooled to 0°C. After that compound **2** (8.14 g, 0.039 mol) was added slowly to this cold mixture. The reaction was stirred at room temperature for 48h. After that the mixture was poured into ice water (200 ml). The precipitate of **PN1** was filtered, washed with H₂O and dried at 100 °C in vacuum. Then, it was crystallized in both cold water and EtOH (**PN1-a**, **PN1-b**). Yield: 3.3 g (50%), mp: 158°C. FT-IR: ν , cm⁻¹ 3200-2400 (COH), 2238 (-C=N-), 1698 (C=O), 1434, 1290, 1214, 765. ¹H NMR (500 MHz, DMSO-*d*₆, δ ppm): 8.52 (s, 1H, ArH), 8.36-8.34 (d, 2H, ArH), 8.27-8.25(d, 2H, ArH), 4.0 (OH). ¹³C NMR (500 MHz, DMSO-*d*₆, δ ppm): 165.15 (C=O). 136.10, 135.01, 134.51,

118.50, 116.03, 115.87. UV-Vis (THF): λ_{max} , nm 453, 365, 301, 291, 244. ESI-MS: calcd: 172.14; found: 171.00 [M]⁺

4-((3,4-dicyanophenyl) ethynyl) benzoic acid (PN2). Iodophthalonitrile (540 mg, 2.12 mmol), 4-ethynyl benzoic acid (360 mg, 2.46 mmol) CuI (19mg) and Pd(PPh)₃Cl₂ (148 mg, 0.211 mmol) were dissolved in 10 ml toluene and 6 ml TEA under argon atmosphere. The reaction mixture was refluxed at 90°C for 24h. After that 10 ml of 15% NH₄Cl solution was added to the reaction mixture. This aqueous mixture was extracted with Et₂O (100 mlx3). The organic layers were separated and dried over Na₂SO₄ and filtered. The solvent was evaporated, and the orange solid was purified by column chromatography on silica gel using CH₂Cl₂: EtOH /(50:1, 40:1 30:1 10:1, 5:1) mixtures as eluent, affording PN2 as a light yellow solid. The white solid was crystallized in EtOH. Yield: 338 mg (58%), mp: 235 °C. FT-IR: v, cm⁻¹ 3200-2400 (-COH), 2240 (-C≡N-), 2231 (-C≡C-), 1674 (-C=O), 1603, 1556, 1486, 1404, 1318, 1298, 1283, 1210, 1176, 1142, 1125, 1112, 1017, 943, 908, 864, 844, 767, 694. ¹H NMR (500 MHz, DMSO-d₆): δ ppm = 8.42 (s, 1H, ArH), 8.21 (d, 1H, ArH), 8.11(d, 1H, ArH), 8.01 (d, 2H, ArH), 7.74 (d, 2H, ArH.). $^{13}\mathrm{C}$ NMR (125 MHz, DMSO-d_6, δ ppm): 167.01 (CO), 136.70 (ArCH), 134.71 (ArCH), 132.24 (ArCH), 130.04 (ArCH), 127.79 (ArC), 125.30 (ArC), 115.51 (-C≡N-), 114.31 (ArC), 94.12 (-C≡C-), 88.80 (-C=C-). UV-Vis (THF): λ_{max} , nm: 330, 308, 250. MALDI-TOF-MS: m/z calcd: 272.26; found: 272.82 [M]+

2.3. X-ray data collection and structure refinement

Data were obtained with Bruker APEX II CCD three-circle diffractometer. Indexing was performed using APEX2 [13]. Data integration and reduction were carried out with SAINT [14]. Absorption correction was performed by multi-scan method implemented in SADABS [15]. The structure was solved using SHELXT [16] and then refined by full-matrix least-squares refinements on F^2 using the SHELXL [16] in Olex2 Software Package [17]. The positions of all H-atoms bonded to carbon and oxygen atoms were geometrically optimized. Finally, their displacement parameters were set to isotropic thermal displacements parameters $(U_{iso}(H)=1.2 \times U_{eq}$ for CH and CH₂ groups or $(U_{iso}(H)=1.5\times U_{eq}$ (-OH). The contribution of seriously disordered EtOH molecules in PN1-a and PN2 was eliminated from the structure using SQUEEZE subroutine [18] in the PLATON software. Crystallographic data and refinement details of the data collection are given in Table 1. Crystal structure validations and geometrical calculations were performed using Platon software [19]. Mercury software [20] was used for visualization of the cif files. Additional crystallographic data with CCDC reference numbers 1435210 (PN1-a), 2031063 (PN1-b), and 1435211 (PN2) have been deposited within the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/deposit.

2.4. Computational methodology

Geometry optimizations were performed using density functional B3LYP [21,22] as implemented in Gaussian 09 [23]. The basis set 6-311++G(d,p) was employed which is widely used for the medium and large systems with hydrogen bonds [24]. Molecular structure visualizations and DFT based analysis were rendered using GaussView 5.0 [25]. The interaction energy for the dimer formations of the structures was corrected for the basis set superposition error (BSSE) with the counterpoise method [26]. The fundamental vibrational frequencies of the monomer and dimer forms of **PN1-a** and **PN2** were examined on the optimized structures and the determination of the vibration modes with potential energy distribution (PED) analysis was performed by using VEDA 4 [27]. In the calculations of vibrational frequency, to prevent possible systematic errors; the values higher than 1700 cm⁻¹ were scaled by 0.958 while those less than 1700 cm⁻¹ by 0.983 for 6-311++G(d,p) basis set [28]. UV-Vis spectral parameters; excitation energies, wavelengths of maximum absorbance (λ), oscillator strengths (f) of monomer and dimer PN structures were investigated with Time-Dependent Density Functional Theory (TD-DFT) at the same level of theory. Solvent effect based on conductive-like polarizable continuum model (CPCM) [29,30] was examined using the Self-Consistent Reaction Field (SCRF) method in the gas phase $(\varepsilon = 1)$, nonpolar-chloroform (CHCl₃) ($\varepsilon = 4.71$) and polar aprotictetrahydrofuran (THF) (ε =7.42). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies known as Frontier Molecular Orbitals (FMOs) and the orbital distributions were examined at the same theoretical level and in the gas phase for monomer PN structures. The density of states (DOS) graph for structures, major and minor contribution to electronic transition at UV-Vis analysis was rendered with GaussSum 3.0 program [31]. In addition, to predict reactivities of molecular structures, some global reactivity descriptors were calculated with TD-DFT/B3LYP at the same basis set.

The ionization potential (I) and electron affinity (A) were taken as approximate I \approx -E_{HOMO} and A \approx -E_{LUMO} by utilizing Koopmans' theorem which provides an alternative method with HOMO-LUMO orbital energies of optimized neutral molecules [32]. To get information about global reactivity behaviors as a whole for PN structures; some parameters such as χ ; electronegativity ($\chi = (I+A)/2$), η ; chemical hardness ($\eta = (I-A)/2$), S; chemical softness ($S = 1/\eta$), μ ; chemical potential (μ =-(*I*+A)/2) and ω ; electrophilicity index $(\omega = \mu^2/2\eta)$ were investigated [33-35]. In addition to global reactivity descriptors, the individual reactivity behaviours of the atoms forming the molecular structure were examined by calculating the local reactivity descriptors known as Fukui functions. In local reactivity descriptors, the atomic charges q_k values of the k atom of the molecular structure were obtained in (N), (N+1), (N-1) neutral, anionic and cationic states according to Natural Population Analysis (NPA) [36]. The condensed Fukui functions were calculated using the UCA-FUKUI v.2.1 software [37] and determined using the finite difference method to obtain electrophilic, nucleophilic and radical attack sites of the PN structures by the formulas [38].

$$f_k^+ = q_k(N+1) - q_k(N)$$
, for nucleophilic attack (1)

$$f_k^- = q_k(N) - q_k(N-1)$$
, for electrophilic attack (2)

$$f_k^0 = [q_k(N+1) - q_k(N-1)]/2$$
, for radical attack (3)

In addition, to determine the reactivity of a field in a molecule against a nucleophilic or electrophilic attack; which defined as dual descriptor was calculated with;

$$\Delta f_k = f_k^+ - f_k^- \tag{4}$$

the equation [39]. It is possible to relate the nonlinear optical properties of molecular structures to their response to the presence of an external electric field. The energy of a neutral molecule in a homogeneous and weak electric field is expressed as follows [40]:

$$E(F) = E(0) - \sum_{i} \mu_{i}F_{i} - \frac{1}{2!}\sum_{ij} \alpha_{ij}F_{i}F_{j} - \frac{1}{3!}\sum_{ijk} \beta_{ijk}F_{i}F_{j}F_{k}$$
$$- \frac{1}{4!}\sum_{ijkl} \gamma_{ijkl}F_{i}F_{j}F_{k}F_{l} - \dots$$

where, E(0); F_i indicates the value of the unperturbed energy and the external field along the i-th direction, μ_i ; dipole moment, α_{ij} , β_{ijk} , γ_{ijkl} ; the components of polarizability, the first-order hyperpolarizability and the second-order hyperpolarizability tensors, respectively. The *i*, *j*, *k*, *l* subscripts denote Cartesian components and

Table 1Crystal data and refinement parameters for PN1a-b and PN2.

Compound	PN1-a	PN1-b	PN2
CCDC Number	CCDC 1435210	CCDC 2031063	CCDC 1435211
Empirical Formula	$C_9H_4N_2O_2$	$C_9H_6N_2O_3$	C ₃₆ H ₂₂ N ₄ O ₅
Formula weight (g. mol ⁻¹)	191.14	190.16	590.57
Temperature (K)	293	299	173
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	Pccn	P2 ₁ /c	P-1
a (Å)	13.9507(3)	3.74870(10)	9.7732(12)
b (Å)	20.4746(4)	13.5864(5)	11.7106(14)
c (Å)	13.3456(3)	17.7883(7)	14.5356(18)
$\alpha(^{\circ})$	90	90	79.125(7)
$\beta(^{\circ})$	90	90.579(3)	75.930(7)
$\gamma(^{\circ})$	90	90	66.012(6)
Crystal size (mm)	$0.283 \times 0.238 \times 0.066$	$0.522 \times 0.102 \times 0.096$	$0.461\times0.243\times0.237$
V (Å ³)	3811.97(14)	905.94(5)	1466.7(3)
Z	16	4	2
$\rho_{\rm calcd} \ (\rm g.cm^{-3})$	1.332	1.394	1.337
μ (mm ⁻¹)	0.100	0.108	0.091
F(000)	1552	392	612
heta range for data collection (°)	2.3-27.5	2.3-25.8	2.3-26.9
Hkl	-16/16, -24/24, -15/15	-4/4, -16/16, -21/21	-11/11, -13/13, -17/17
Reflections collected	27844	9628	17664
Independent reflections	3349 [R(int) = 0.0624]	1577 [R(int) = 0.0702]	5166 [R(int) = 0.0404]
Data/restraints/parameters	3349/0/237	1577/0/136	5166/0/381
Goodness-of-fit on F ²	1.070	1.075	1.061
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0491$, $wR_2 = 0.1305$	$R_1=0.0489,wR_2=0.1309$	$R_1 = 0.0471$, $wR_2 = 0.1212$
R indices (all data)	$R_1 = 0.0699$, $wR_2 = 0.1377$	$R_1=0.0648,wR_2=0.1432$	$R_1 = 0.0707$, $wR_2 = 0.1335$
Largest diff. peak and hole $(e.Å^{-3})$	0.24 and -0.20	0.17 and -0.27	0.45 and -0.20

a repeated subscript means summation over the x, y, z indices. While determining the potential of **PN1-a** and **PN2** monomer structures to be non-linear optical material; total static dipole moment (μ_{tot}), mean polarizability ($< \alpha >$), anisotropic of the polarizability ($\Delta \alpha$) and total first-order hyperpolarizability (β_{tot}) parameters were obtained in terms of cartesian coordinate components with the following equations [41,42]:

$$\mu_{\text{tot}} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$$
(5)

$$\langle \alpha \rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \tag{6}$$

$$\Delta \alpha = \frac{1}{\sqrt{2}} \Big[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 \\ + 6 \Big(\alpha_{xz}^2 + \alpha_{xy}^2 + \alpha_{yz}^2 \Big) \Big]^{1/2}$$
(7)

$$\beta_{\text{tot}} = \left[\left(\beta_{\text{xxx}} + \beta_{\text{xyy}} + \beta_{\text{xzz}} \right)^2 + \left(\beta_{\text{yyy}} + \beta_{\text{yzz}} + \beta_{\text{yxx}} \right)^2 + \left(\beta_{\text{zzz}} + \beta_{\text{zxx}} + \beta_{\text{zyy}} \right)^2 \right]^{1/2}$$
(8)

The change of some thermodynamic parameters such as heat capacity, $(C_{p,m}^0)$, entropy, (S_m^0) , and enthalpy change (ΔH_m^0) were examined in the range of 100-800 K for **PN1-a** and **PN2** monomers.

2.5. Investigation of film formation of PN1 and PN2

The crystals synthesized within the scope of the project will be dissolved by dissolving in suitable solvents and coated by ITO (indium tin oxide) andsilverwas evaporated approximately 100 nm thickness on **PN1** and **PN2** coated substrates. To evaporate the remaining solution, the samples were dried and annealed at 110°C for 10 minutes. The spin coating speed is 2000 rpm. The ITO substrates to be used during the construction of the diodes were cleaned with sonic vibrator in isopropanol and acetone for 10 minutes, respectively. Obtained films were annealed at 110 °C to remove residual solvents. It was given schematic structure of diode with **PN1** and **PN2** in Fig. S.3.

3. Results and discussion

3.1. Synthesis and characterization

PN1 was synthesized in three steps starting from trimellitic anhydride [43]. **PN2** was prepared by a Sonogashira catalytic crosscoupling reaction with 4-iodophthalonitrile and 4-ethynyl benzoic acid by using $Pd(PPh_3)_2Cl_2$ catalyst in the presence of Cul/Et_3N [44]. The synthetic route to phthalonitrile derivatives were depicted in Scheme 1.

Phthalonitrile derivatives were fully characterized by spectroscopic techniques, including NMR, UV-Vis, FT-IR, X-ray, mass spectrometry (MS). These compounds exhibited high solubility in common organic solvent such as ethyl alcohol, dichloromethane, DMSO, CHCl₃.

3.2. X-ray crystallography

The solid-state structures of **PN1-a**, **PN1-b** and **PN2** were determined using single-crystal X-ray structural analysis. Suitable crystals for X-ray diffraction study of **PN1-a** and **PN2** were grown via recrystallization from ethyl alcohol.

Interestingly, the second form of 3,4-dicyanobenzoic acid, which was re-crystallized via ethyl alcohol-water, was isolated. **PN1-a**, **PN1-b**, and **PN2** were crystallized from the different crystal systems, which are orthorhombic *Pccn*, monoclinic $P2_1/c$, and triclinic *P*-1, respectively. Details of the data collection conditions and the parameters of the refinement process of **PN1a-b** and **PN2** in Table 1. While the asymmetric unit of **PN1-b** includes only one molecule, the asymmetric unit of **PN1-a** and **PN2** consists of two phthalonitrile molecules. In all compounds, the carboxylic acid and



Scheme 1. Synthesis of phthalonitrile derivatives PN1 and PN2.



Fig. 2. (A) The OPTEP drawings of **PN1-a** molecular structure with the atomic numbering scheme (B) The perspective view of classical carboxylic acid inversion dimer with R2²(8) motif in **PN1-a** (C) The 2D hydrogen bonded layers formed by intermolecular CH…N interactions (D) View of the 2D inclined interpenetration observed in **PN1-a**.

phthalonitrile moieties almost lie in the plane of the benzene ring as indicated in Fig. 2A, 3A, and 4A.

The C=N bond lengths (1.139(3) Å-1.150(3) Å for **PN1-a**, 1.140(3) Å for **PN1-b**, and 1.139(3) Å-1.142(2) Å for **PN2**) are in good agreement with our previously reported structures [45-49]. In **PN1-a**, molecules are connected by a pair of classical O-H···O hydrogen bonds (O15···O33=2.608(2) Å, O32···O16= 2.596(2) Å) forming classical carboxylic acid inversion dimers showing an R2²(8) motif (Fig. 2B). Furthermore, these interactions are accompanied by non-classical CH···N interactions (C26···N13=3.377 Å and C4···N31=3.463 Å) to form 2D hydrogen bonded layers.

The layers contain windows (Fig. 2C), which are large enough to allow mutual inclined interpenetration as shown in Fig. 1D. On the other hand, no-classical inversion dimer was observed in **PN1-b**. **PN1-b** is stabilized by classical intermolecular hydrogen bonding interactions (O17 \cdots O8=2.640(3) Å, O8 \cdots N1=2.999(3) Å, O8 \cdots N15=2.933(3) Å) to form 2D hydrogen bonded network (Fig. 3B, 3C).

The resulting 2D layered network is expanded into a 3D supramolecular network by intermolecular $\pi \cdots \pi$ stacking interactions (3.371 Å in Fig. 4D). As in **PN1-a**, molecules in **PN2** are linked by a pair of O-H \cdots O hydrogen bonds (O2 \cdots O3=2.644(2) Å) to form classical carboxylic acid inversion dimers showing an R2²(8) motif (Fig. 4B). Crystal structure is stabilized by a combination of intermolecular π - π interactions between 3.682 Å-3.874 Å (Fig. 4C and 4D).

3.3. Optimized molecular geometry

The optimized monomer and dimer structures of PN1-a, PN1**b** and **PN2** are depicted in Fig. S.4. The values of uncorrected total energy, counterpoise-corrected energies, BSSE corrected interaction energy and dipole moments are given in Table S.1 for monomer and dimer structures. The resulting energy values of the dimeric PN structures point out that they are more stable than their monomeric ones. The corrected hydrogen bonded interaction energies ($\Delta E = E_{dimer} - 2E_{monomer}$) of dimer structures formed by the interaction of hydrogen bonds between homonuclear molecules are -14.57 kcal/mol for PN1-a, -29.49 kcal/mol for PN1-b and -18.64 kcal/mol for PN2. The dipole moment value of the PN1-b optimized dimer structure formed by the hydrogen bond interaction between water molecules and the carboxylic acid group is 0.0076 Debye, while that of the monomer is 8.8903 Debye. The dipole moments of PN1-a and PN2 monomers are 5.5501 Debye and 7.8105 Debye, while are 0.0021 Debye and 0.0019 Debye for dimers. The almost zero dipole moment values of the dimeric structures confirm that there is a centrosymmetric cyclic dimer formation [50].

Since the dimerization is governed by the intermolecular Hbond interactions, some parameters of optimized monomer and dimer structures, particularly the ones involved in H-bond is of interest and therefore some donor (D)-acceptor (A) interactions are tabulated in Table 2. The optimized **PN1-a** and **PN2** dimers possess two intermolecular hydrogen-bonds between the hydroxyl group



Fig. 3. (A) The OPTEP drawings of **PN1-b** molecular structure (B) The perspective view of classical hydrogen bonding interactions in **PN1-b** (C) The 2D hydrogen bonded layers formed by intermolecular O-H-O interactions (D) View of the intermolecular $\pi - \pi$ stacking interactions observed in 3D hydrogen-bonded network of **PN1-b**.



Fig. 4. (A) The OPTEP drawings of **PN2** molecular structure (B) The perspective view of classical carboxylic acid inversion dimer with $R2^2(8)$ motif in **PN2** (C) and (D) View of the intermolecular $\pi \cdot \cdot \pi$ stacking interactions observed in **PN2**.

(O-H bond) acting as a donor and the carbonyl oxygen (C=O) acting as an acceptor. The optimized **PN1-b** dimer structure is formed by the hydrogen bond interaction between the oxygen of the water molecule which acts as an acceptor and the hydroxyl group as the donor. With the DFT approach, D…A distances are equal to 2.66 Å for structures. The calculated distances are within the expected range of 2.5-3.2 Å [51] for strong hydrogen bond interactions. In addition, the intermolecular hydrogen bond (O-H…O) angle are almost linear (179.8°, 178.0° and 178.9° **PN1-a, PN1-b** and **PN2**, respectively).

Some selected bond distances are tabulated in Table S.2 comparison to the crystallographic data and more structural parameters are given in Table S.3.

The carbonyl bond distance is computed as 1.227 Å for **PN1-a**, 1.214 Å for **PN1-b**, 1.231 Å for **PN2** dimer structures, whereas these distances are 1.206 Å, 1.205 Å 1.208 Å for their monomer structures, respectively. In optimized dimer structures, C–O single bond lengths are 1.317 Å for **PN1-a**, 1.326 Å for **PN1-b**, 1.322 Å for **PN2**. For monomer structures, respectively, these bond lengths are 1.351 Å, 1.351 Å and 1.356 Å. Hydroxyl group bond length is obtained as \approx 0.96 Å for the monomeric structures, \approx 1.00 Å for dimer ones.

The carbon-nitrogen triple bond lengths of the nitrile group are 1.153 Å-1.155 Å for both monomer and dimer forms of **PN** structures. This bond length for phthalonitrile group was calculated as 1.154 Å with the basis set of 6-311G(d,p) [52] and with the basis set of 6-311++G(d,p) as 1.155 and 1.156 Å [53]. The alkyne group bond length of the **PN2** structure, the DFT value estimated is 1.210 Å in both the monomeric and dimeric forms. The aromatic ring C-C bond distance values are in the range of 1.387-1.412 Å for monomer, 1.388-1.414 Å for dimer in the **PN1-a**, 1.389-1.414 Å for monomer, 1.390-1.413 Å for dimer in the **PN1-b**, 1.385-1.413 Å for both monomer and dimer in the **PN2**.

Carboxylic acid group O=C-O bond angles are known to be trigonal planar with about 120° bond angles and the calculated values for **PN** structures follow this expectation. For **PN1-a, PN1-b** and **PN2** structures these angles are obtained as 123.1°, 123.2°, 122.2° at the monomer forms and 124.0°, 124.3°, 123.0° at the dimer forms, respectively. In addition, the C–O–H bond angles are determined as 107.4°, 107.45°, 106.9° in PN monomer structures and 110.5°, 109.7°, 110.3° in dimer structures. The theoretical -N=C–Cbond angles in **PN** structures monomer and dimer forms are very close to each other approximately 179° and have a value that sup-

Table 2

Some selected intermolecular hydrogen bonding geometry (Å, °) parameters for the dimeric structures of **PN1a-b** and **PN2**.

	D—H…A	D—H	H…A	D…A	D−H…A		
PN1-a							
XRD	015-H15-033	0.820(2)	1.796(2)	2.608(2)	170.83(2)		
DFT		1.000	1.666	2.667	179.868		
XRD	033-H34015	0.819(2)	1.793(2)	2.596(2)	165.88(2)		
DFT		1.000	1.667	2.667	179.856		
PN1-b							
XRD	017-H1708	0.820(3)	1.821(3)	2.640(3)	176.51(3)		
DFT		1.000	1.666	2.666	178.069		
PN2							
XRD	02-H203	0.841(2)	1.800(2)	2.644(2)	174.42(2)		
DFT		0.999	1.665	2.665	178.957		
XRD	04-H4…01	0.841(2)	1.800(2)	2.644(2)	174.42(2)		
DFT		0.999	1.665	2.665	178.957		

ports the linear geometry of the cyano groups. For dimers, carbonyl and hydroxyl bonds are elongated, while C–O single bond lengths are shorter compared to monomers.

A similar deviation was observed for the O=C-O and C-O-H bond angles of **PN** structures, as the values are larger in dimers than the monomer ones. Similar effects of dimerization on these geometrically parameters were also reported in previous studies for molecular groups containing the –COOH moiety [54-57]. Furthermore, it has been observed that dimerization does not cause a significant alteration in the aromatic ring and cyano groups of PN structures and alkyne group parameters for **PN2**.

As can be seen in Table S.2 and Table S.3, the differences between monomeric and dimeric species originating mainly from the carboxylic group are also confirmed by XRD data. Some discrepancies between XRD analysis and results obtained from DFT approach; it results from the fact that molecular structures being in the solid phase in the experimental process, and at the gaseous phase throughout the theoretical analysis process.

3.4. IR analysis

IR spectral characterization of **PN1-a** and **PN2** structures was performed by DFT and PED analysis together based on the monomeric and dimeric formations. Experimental FT-IR spectra in Fig. S.5 and simulated ones with at DFT/B3LYP/6-311++G(d,p) level for monomer and dimer PN structures are illustrated in Fig. S.6. All the spectral and scaled wavenumbers, potential energy distributions (PED) and the assignments of the basic vibration modes obtained for the monomer and dimer structures of PN are given in Table S.4, Table S.5 as a summary of some selected results.

PN1-a monomer structure which consists of 17 atoms has a total 45 fundamental vibration modes of which 16 stretching, 19 bending and 10 torsion vibrations. For **PN2** monomer structure with 29 atoms, there are 28 stretching, 33 bending and 20 torsion vibrations of 81 fundamental vibration modes. Structures have no imaginary frequency value. Dimeric structures of **PN1-a** and **PN2** have a centrosymmetric dimer feature formed by intermolecular O-H…O hydrogen bonds. Consequently, correspond to each vibration mode two wavenumbers that are quite close to each other in most cases have been obtained for the dimer structures.

The presence of the carboxylic acid moiety can be confirmed in the infrared spectra by absorption bands of hydroxyl and carbonyl groups. Although O-H stretching absorption appears with alcohols, and C=O stretching absorption appears within the expected range of regions for aldehydes and ketones in the spectra, the shifts in wavenumbers and the tendency of more widening of the peaks emerge as characteristic features of carboxylic acid [58]. O-H stretching vibration observed in the range of 3670-3580 cm⁻¹ for alcohols, while it is at 3580-3500 cm⁻¹ for the free or monomer form of carboxylic acid, it appears in the region of 3300-2500 cm⁻¹ for dimer formed by hydrogen-bonded interaction [59,60]. O-H stretching peaks in the FT-IR spectrum for both PN structures were observed in a quite broad range of at 3200-2400 cm⁻¹ centred near 2800 cm⁻¹ due to its overlapping with the aromatic group C-H absorption. Calculated at 3604 and 3611 \mbox{cm}^{-1} with the contribution of pure 100% PED for monomer forms of PN1-a and PN2 structures, this band at 3025, 2965 cm⁻¹ and 3023, 2966 cm⁻¹ for their dimeric forms, respectively. While the theoretical values indicate the absorption of OH group that non-hydrogen bonding almost located at 3600 cm⁻¹ for monomer structure forms of PN1-a and PN2, the shifting of absorption to lower frequency values approximately >500 cm⁻¹ exist the presence of a stable dimeric form characterized by an intermolecular hydrogen bond of O-H…O type.

It is known that the C=O stretching vibration, which is one of the important absorption bands of the double bond region of the spectrum, can take specific values depending on conjugation, properties of substituents, and inter and intra-molecular hydrogen bond interactions [55,61]. In the case of carboxylic acid, the carbonyl peak appearing as a dense band according to the presence of saturated or unsaturated and even hydrogen bond in the region range of 1760-1690 cm⁻¹, in the dimer formations somewhere near at 1700 cm^{-1} , and in the monomer formations at about 1760 cm^{-1} it is expected [59]. In the FT-IR spectrum, C=O stretching vibration was observed as a sharp peak at 1698 cm⁻¹ for PN1-a and 1674 cm⁻¹ for **PN2**. On the other hand, this peak is computed theoretically as 1722 cm⁻¹ for **PN1-a** monomer structure, 1652, 1639 cm⁻¹ for its dimer structure (with contribution of the pure 85% PED), 1711 cm⁻¹ for monomer structure of **PN2**, 1661, 1632 cm⁻¹ was obtained for its dimer structure (with contribution of the pure 82% PED). It shows that the C=O stretching vibrations calculated for the dimeric forms of the PN structures shifted to low-frequency values compared to the monomer ones. Other important bands exhibited by the carboxylic group which often overlapped with other absorptions in the fingerprint region of the molecular structures; are C-O stretching, in-plane and out-of-plane bending vibrations associated with O-H components.

The expected range in the spectrum for C-O stretching and O-H in-plane bending coupling band is about 1440-1395 cm⁻¹ region in dimeric species, while O-H in-plane and C-O stretching vibrations appear at 1380-1280 cm^{-1} and 1190-1075 cm^{-1} in monomer ones, respectively [59,62]. C-O stretching and COH inplane bending vibrations were determined at 1347 cm⁻¹ with 19% and 30% PED contribution, respectively, for monomer PN1-a (1461, 1422 \mbox{cm}^{-1} for dimer structure) and at 1340 \mbox{cm}^{-1} with 16% and 35% PED contribution for monomer **PN2** (for 1451, 1422 cm⁻¹ for dimer structure). Spectrally, this band was observed at 1434 cm⁻¹ and 1404 cm⁻¹ for structures. C-O bond stretching vibrations observed together with other HCC, CCC, bending vibration modes are 1165, 1105 and 1080, 1017 cm⁻¹, respectively for **PN1-a** and **PN2** monomer structures. Scaled wavenumbers in which C-O vibration was observed for dimeric structures formed by O-H--O type hydrogen bond interaction; are 1186 cm⁻¹, 1132;1130 cm⁻¹ for PN1**a**, respectively, 1120 cm⁻¹, 1013 cm⁻¹ for **PN2**, respectively. Other in-plane and out-of-plane deformation vibration modes associated with the carboxylic acid group are given in Table S.4.

The descriptive peak for the presence of cyano groups in the triple bond region is expected in the range of 2200-2400 cm⁻¹ [63]. The $-C \equiv N$ - stretching vibration appeared as 2238 cm⁻¹ for **PN1-a** and 2240 cm⁻¹ for **PN2** structures as sharp and in medium intensity peaks in the FT-IR spectrum. This peak in **PN1-a** structure was theoretically calculated with pure 65% PED value as

2244 and 2240 cm⁻¹ for the monomer, 2238 and 2236 cm⁻¹ for the dimer. In case of PN2; it was determined as 2243/2236 cm⁻¹and 2236/2229 cm⁻¹ for monomer/dimer structure with 85% and 84% pure PED contribution, respectively. The characteristic -C=N- stretching vibration for the phthalonitrile part was reported as spectral 2233 cm⁻¹ [64], 2235 cm⁻¹ [65], 2229-2236 cm⁻¹ [66]. Hence, it can be concluded that the spectral values of CN stretching band marked for PN structures are compatible with the typical \approx 2300 cm⁻¹ value expected for phthalonitrile groups. It is clear that the theoretical values were obtained higher than the experimental ones, a similar situation was observed in the studies that reported CN stretching vibration as 2234-2342 cm⁻¹ [67] and 2258 cm⁻¹ [68] with the DFT approach. $-C \equiv C$ - stretching vibration frequency of the PN2 structure was assigned as a medium intensity peak at 2231 cm⁻¹ in FT-IR spectra, whilst it was computed as 2202 cm⁻¹ with a pure 81% PED value in both the monomeric and dimeric form. The expected frequency range for the alkyne group stretching vibrations which known to have a small dipole moment change is the region of 2260-2100 cm^{-1} of the spectrum [60]. The obtained spectral and theoretical values for this stretching band in the **PN2** structure are within the expected frequency range.

The presence of the –COOH group contained in the **PN1-a** and **PN2** structures and its tendency to the dimeric formation, showed its effect in some wavenumber values. It is determined to shift to lower frequency values on dimer forms of structures that approximately <500 cm⁻¹ for the O-H stretching vibrations, in the range of 70-100 cm⁻¹ for the C=O stretching vibrations. Similar results based on the effect of dimerization were observed in some studies reported for molecular structures containing -COOH moiety [54,56,69,70]. While the effects of hydrogen bonding interaction are noticed in the wavenumbers obtained for monomer and dimer structures, there are some differences between experimental and theoretical values.

3.5. UV-Vis analysis

The nature of the electronic transitions of PN structures was investigated by UV-Vis spectral analysis, which plays a key role in the determination of optically active materials. The electronic absorption spectra of the structures in THF and CHCl₃ at 1×10^{-5} M concentration value in the range of 200-600 nm are given in Fig. S.7 and S.8 With a theoretical approach at framework TD-DFT/B3LYP/6-311++G(d,p) for the monomer and dimer structures of **PN1-a** and **PN2** some electronic absorption spectral parameters have examined in mentioned solvents and gas phase and results are tabulated in Table S.6.

Frontier molecular orbitals are crucial for the identification process of electronic transitions in UV-Vis spectral analysis. HOMO-LUMOs together with DOS diagrams for PN monomers are given in Fig. S.9, diagrams of molecular orbital other contributing to transitions are presented in Fig. S.10. DOS diagrams shaped with Gaussian curves which of unit height and the stated full width at halfmaximum [31], have used as an effective tool for visualizing the contributions of molecular orbitals, and also the band gap of PN structures. As shown in Fig. S.10, HOMO is located on the all phthalonitrile moiety with a small part over the oxygen atom of the carbonyl group, while LUMO is located over almost the entire molecular structure for PN1-a monomer. For PN2 monomer; the large density of HOMO is localized on the ethynylbenzoic acid and on the phthalonitrile group except for the nitrile group, while the LUMO localized symmetrically over almost the entire molecular skeleton.

The electronic absorption spectrum of **PN1-a** structure displays three absorption peaks in the near UV region at 246, 292 and 303 nm in the CHCl₃, while five absorption peaks in the near UV and visible region at 244, 291, 301, 365 and 453 nm for THF sol-

vent. Corresponding to the peaks having maximum absorbance intensity in the spectrum, the λ_{max} values determined by the TD-DFT approach are 259/264 nm in CHCl₃, 259.23/263.76 nm in THF medium in order of monomer/dimer. These maxima point out HOMO \rightarrow LUMO transition with major contribution values of 61%-69%. It is known that phthalocyanines have two strong characteristic electronic absorption bands. One of which is the Soret or B band observed at the near UV region in the range of 300-400 nm and the other one is the Q band observed in the range of 600-700 nm at the visible region [71]. The absorption wavelengths of 365 and 453 nm in the THF medium of the **PN1-a** can be the peaks corresponding to the B and Q bands.

The absorption peaks recorded for CHCl₃ and THF solvent media in the UV spectrum of the **PN2** structure are 250, 312, 333 nm and 250, 308, 330 nm, respectively. As can be seen in Table S.6, λ_{max} values which have high oscillator strength indicate HOMO \rightarrow LUMO transition with major contribution value of 99% are 362.24 nm in CHCl₃ and 362.10 nm in THF for the monomer structure. The λ_{max} values indicating the same possible transition with major contribution values of 61% are 366.81nm in CHCl₃ and 366.84 nm in THF for the dimeric state.

It was determined that spectral absorption bands (except 365 and 453 nm) blue-shifted ~2nm for **PN1-a** structure and ~3-4 nm for **PN-2** structure due to an increase the solvent polarity (from CHCl₃ to THF). Unlike the **PN1-a** structure, the structure of **PN2** contains an alkyne group that will cause the increase of π -electron density within the molecular structure so the **PN2** structure has longer absorption wavelengths and lower excitation energy values than the **PN1-a** structure. Furthermore, it was observed that the λ_{max} values calculated for dimer forms with the TD-DFT approach were higher than monomers. According to the spectral values determined , the hypochromic effect observed in the transition from non-polar to polar aprotic solvent is more prominent just in the **PN1-a** structure.

3.6. Reactivity descriptors of structures

The abilities of molecular systems to donate and accept electrons can be associated with their HOMO and LUMO energy values. In particular, the difference between HOMO and LUMO energy values ($\Delta E = |E_{HOMO}| - |E_{LUMO}|$) of the structures, i.e. the energy band gap, contains important clues about the stability of the molecular structures. The values of FMOs energies and some reactivity parameters for the **PN1-a** and **PN2** monomer structures were obtained at TD-DFT/B3LYP/6-311++G(d,p) level of theory in the gas phase (Table S.7).

The donor-acceptor characteristic properties can be evaluated with the HOMO and LUMO energy values, the ionization potential (*I*) and electron affinity (*A*) parameters. Low (*I*) value can be associated with a good electron donor ability while a high electron affinity (*A*) value with a good electron acceptor ability. **PN2** monomer, which has a higher HOMO energy and a lower ionization potential (*I*=7.115 eV), draws attention with a better electron donor character, while **PN1-a** monomer structure exhibits a lower LUMO energy and a higher electron affinity (*A*=3.371 eV) and therefore can be considered asa better electron acceptor. The difference between the HOMO and LUMO energies of the structures has been calculated as 5.015 eV for **PN1-a** monomer and 3.843 eV for **PN2** monomer. Lower ΔE value in **PN2** monomer may indicate a stronger intramolecular charge transfer compared to **PN1-a** monomer.

Global reactivity descriptors; such as electronegativity (χ), chemical hardness (η), chemical softness (S), chemical potential (μ) and electrophilicity index (ω) values are other parameters that determine the reactivity of the molecular system. Chemical potential (μ) defined as a negative value of electronegativity measures the escaping tendency of electron from the equilibrium sys-

tem [33]. The concepts of global chemical hardness and softness, which are a measure of charge transfer, contributing to the development of hard-soft acids and bases (HSAB) theory qualitatively, provide an insight into the stability of molecular systems. Calculated χ , η and S values are 5.878 eV, 2.507 eV and 0.398 eV⁻¹ for the PN1-a monomer, 5.193 eV, 1.921 eV and 0.520 eV^{-1} for the PN2 monomer, respectively (Table S.7). PN2 monomer has a higher global chemical softness value than PN1-a monomer structure, which indicates that it has a soft molecular structure. Soft molecules can be more reactive and more polarized; therefore, intramolecular charge transfer can be directed much more easily. The fact that PN2 has a narrower HOMO-LUMO gap compared to PN1-a supports this result. The other parameter commonly used in chemical reactivity analysis is the global electrophilicity index (ω) descriptor that determines the energy change of an electrophile when it is saturated with electrons and classifies electrophilic structure quantitatively at a relative scale [35,72].

The molecular structure depending on whether the value of ω less than 0.8 eV is, between 0.8 to 1.5 eV and greater than 1.5 eV, can be evaluated as marginal, medium and strong electrophile, respectively [73]. The calculated ω values for PN monomers (6.891 eV for **PN1-a**, 7.015 eV for **PN2**) show that both can be considered as strong electrophiles. However, **PN2** monomer with a lower η (1.921 eV), higher μ (-5.193 eV) and ω (7.015 eV) values shows a better electrophilic character than **PN1-a** monomer.

In order to determine the local field reactivity and site selectivity of PN structures, Fukui functions (f_k^+, f_k^-, f_k^0) and dual descriptor values have been calculated (Table S.8). This analysis contributed to the individual investigation of the reactivity tendencies of atoms and provided the prominent reactivity sites to be determined by considering the entire molecular structure. Calculated f_k^+ , f_k^- and f_k^0 values indicate probable regions for nucleophilic, electrophilic and radical attack in molecular structures. According to the results obtained for the structure of PN1-a monomer; higher f_k^+ values are for N13, C3, N14, O16, C8 atoms, higher f_k^- values are for N14, N13, C11, C8, C6 atoms and higher f_k^0 values are N13, N14, C3, C8, C11 atoms. In the case of **PN2** monomer structure, the highest f_k^+ ; f_k^- and f_k^0 values have been obtained for N3, C7, N13, C16, C19; C24, C6, C19, N3, C14 and C24, C6, N3, C7, C19 atoms, respectively. It is also possible to specify the regions prone to electrophilic and nucleophilic attacks by considering the signs of dual descriptors. The graphical representation of dual descriptors is given in Fig. S.11 The dual descriptors with a positive sign ($\Delta f_k > 0$) indicate the favourable site for the nucleophilic attack, whilst those with a negative sign $\Delta f_k < 0$ may point out the potential site for the electrophilic attack. It can be concluded that the carboxylic acid group region may be favoured for nucleophilic attack in the PN1-a monomer, while has a partial potential for both nucleophilic and electrophilic attacks in the PN-2 monomer.

Another tool to get information about reactivity of molecules is to examine electrostatic potential maps which show charge distribution within the molecule with different colour codes according to the electrostatic potential values. The obtained MEP and 2D contour maps for PN structures are illustrated in Fig. 5. The regions having negative electrostatic potential on the molecular surface of PN1-a monomer are around the N13 with the value of -0.0180 a.u., N14 with the value of -0.0183 a.u., O16 with the value of -0.0089 a.u. and O15 with the value of -0.0015 a.u. atoms. In the structure of PN2, negative electrostatic potential is around the atoms of N3, N13, O1 and O2 with values of -0.0252, -0.0237, -0.0157 and -0.0048 a.u. MEP analysis points out that reactivity fields prone to electrophilic attacks for both PN structures may be around these atoms. The negative electrostatic potential value has not been observed at the position of PN monomer structures carbon atoms (0.0039-0.0297 a.u. for PN1-a, 0.0020-0.0151 a.u. for PN2), the green coded areas of the map indicate the region of carbon atoms, which are almost close to zero electrostatic potential. Besides, -COOH moiety carbonyl group atoms; C12 atom (0.0297 a.u.) for **PN1-a** and C28 atom (0.0151 a.u.) for **PN2** atom are those with high positive value compared to other carbon atoms due to the electronegative oxygen atom drawing the electron density over itself. A similar state having positive potential is also valid for the all hydrogen atoms on both structures, the most positive ones were determined for the -OH group H15 atom (0.0334 a.u.) for **PN1-a** monomer and H2 atom (0.0213 a.u.) for **PN2** monomer. The centre of nucleophilic attacks to PN structures may be regions with positive potential values (blue-coded on the map) and particularly where of hydrogen atoms with the highest positive value. Prominent active sites on the MEP and contour map confirm the presence of intermolecular O-H···O hydrogen bond interaction that binds the two monomer structures of **PN1-a** and **PN2**.

When the reactivity analyses for PN structures are evaluated together (Fukui functions and MEP analysis), there is a difference which might result from the fact that the condensed Fukui functions are highly dependent on the population analysis scheme and the basis set selection [74]. Moreover, Fukui functions take into account soft-soft interactions in molecular systems, while MEP describes hard-hard interactions [75].

3.7. NLO analysis

Total static dipole moment (μ_{tot}), mean polarizability ($< \alpha >$), the anisotropic of the polarizability ($\Delta \alpha$) and total first-order polarizability (β_{tot}) values of the **PN1-a** and **PN2** monomer structures were calculated with the Eqs. (5-8) and tabulated in Table S.9. For **PN1-a** ve **PN2** structures, μ_{tot} values were 2.183 Debye and 3.072 Debye, while $<\alpha>$ and $\Delta\alpha$ -components independent and dependent on the direction of the applied electric field- values were obtained as 18.215×10^{-24} esu, 39.867×10^{-24} esu and 15.685×10^{-24} esu, 52.809×10^{-24} esu, respectively. It was determined that PN2 monomer exhibits higher polarizability capability than **PN1-a** monomer. A similar situation is observed in β_{tot} values and calculated as 3030.6×10^{-33} for **PN1-a** and 13394.75×10^{-33} esu for PN2. For the prediction of the potential use as NLO material of molecular structures; β_{tot} values are particularly known to be an important parameter and compared with the urea molecule which is considered as a reference. At the same theoretical level, the β_{tot} value for urea was calculated as 782.99×10^{-33} esu and the $\beta_{tot}/_{(urea)}$ ratio was determined as 3.8 for the **PN1-a** structure and 17.1 for the PN2 structure. The fact that the PN2 structure has a narrow energy gap (ΔE =3.84 eV), a higher chemical softness value ($S=0.52 \text{ eV}^{-1}$) than **PN1-a**, and therefore a higher potential of intramolecular charge transfer also supports this possibility with its high β_{tot} value. In the design of technological products, materials that exhibit NLO properties are remarkable significance at telecommunication, military and scientific environmental monitoring, data storage in information technologies, sensor design, laser and on a wide scale optoelectronic applications etc. areas [76,77]. The obtained results for PN skeletal structures which consist of phthalonitrile moieties with strong π -electron charge density and -COOH with the electron-withdrawing, show that they may have the potential to be used as NLO material in such applications.

3.8. Thermodynamic properties

Characteristic thermodynamic parameters such as heat capacity, $C_{p,m}^0$, entropy, S_m^0 , and enthalpy change, ΔH_m^0 , for the **PN1-a** and **PN2** monomer structures were examined at temperature values ranging from 100K to 800K and at 1 atm pressure with on the basis of vibrational analysis at with B3LYP/6-311++G(d,p) method. The results showing the variation of these parameters with temperature are given in Table S.9 As can be seen in Table S.9, it is



Fig. 5. 3D plot of molecular electrostatic potential map with 0.0004 a.u. isodensity surface from the most negative to the most positive values; in the range of -0.0183 to 0.3340 a.u. for PN1-a, -0.0252 to 0.0213 a.u. for PN2 and 2D contour map diagrams with isovalue: 0.02.

observed an increase in heat capacity, entropy and enthalpy parameters owing to the increase in the vibration intensities with the rising temperature values of the compounds.

The correlation graph showing the variation of the mentioned parameters of **PN1-a** and **PN2** structures with temperature is given in Fig. 6, and the corresponding fitting equations in which every parameter is represented as a function of temperature and their corresponding fitting factors (R^2) are given below. Thermodynamic parameters obtained and their changes with temperature for PN structures may serve in the progression of chemical reactions with

respect the second law of thermodynamics in the thermochemical field applications.

For **PN1-a** structure; $C_{p,m}^{0}(\mathbf{T})=3.64275+0.1416 \ \mathbf{T}$ -7.1969.10⁻⁵ \mathbf{T}^{2} ($R^{2}=0.9997$) $S_{m}^{0}(\mathbf{T})=55.8334+0.17593 \ \mathbf{T}$ -5.70324.10⁻⁵ \mathbf{T}^{2} ($R^{2}=0.9998$) $\Delta H_{m}^{0}(\mathbf{T})=-1.14463+0.01803 \ \mathbf{T}+3.83494.10^{-5} \ \mathbf{T}^{2}$ ($R^{2}=0.9995$) For **PN2** structure; $C_{p,m}^{0}(\mathbf{T})=4.09306+0.24294 \ \mathbf{T}$ -1.18559.10⁻⁴ \mathbf{T}^{2} ($R^{2}=0.9996$) $S_{m}^{0}(\mathbf{T})=66.13689+0.27808 \ \mathbf{T}$ -8.01677.10⁻⁵ \mathbf{T}^{2} ($R^{2}=0.9999$) $\Delta H_{m}^{0}(\mathbf{T})=-1.74222+0.02608 \ \mathbf{T}$ +6.84747.10⁻⁵ \mathbf{T}^{2} ($R^{2}=0.9995$)



Fig. 6. Some thermodynamic parameters of the monomer PN1-a and PN2 structures.

3.9. Electrical conductivity and morphological properties

Conductivity decreases with increasing frequency (Fig. 7a) for **PN1-a** crystal, while for **PN2** crystal, conductivity increases with increasing frequency and it decreases again when it reaches a maximum (Fig. 7b). This situation is related to in-material polarization. The **PN2** structure has high polarizability values than **PN1-a** structure (Table S.10), as well as its high chemical softness value (S=0.52 eV⁻¹) and narrow energy band (ΔE =3.84 eV), also supports this information.

Scanning Electron Microscope (SEM) was used to analyze the morphological properties of the formed films on ITO coated glass substrate. In these images growing trend of the crystalline grains of **PN1** and **PN2** thin films can be observed. As can be seen from SEM images in Fig. 8, homogeneous films were obtained. However, the surface morphology in these images indicated different feature sizes that could be due to different crystal orientations. Thin films of **PN1** and **PN2** were seen to have a wrinkled network structure consisting of dense grains from agglomerated crystal particles and some cracks were observed between wrinkled network structures.

Conclusions

The present paper was primarily designed to characterize the structure of two compounds, monocarboxylic acid substituted phthalonitrile derivatives and to investigate the effects of dimerization due to the presence of the -COOH group, which has a natural tendency to dimer formation. XRD analysis of the crystal structures synthesized revealed the presence of intermolecular hydrogen bonds between the carboxylic acid groups. Theoretical analyses were performed with the DFT approach at the B3LYP/6-311++G(d,p) level in the gas phase for PN structures. The calculated total energy values for optimized molecular geometries with the DFT approach show that dimeric structures shaped by strong hydrogen bond interactions are more stable than monomer ones. The nearly zero dipole moment values for dimeric forms confirm the existence of a centrosymmetric symmetric cyclic dimer formation. The presence of intermolecular interaction even in the gas phase showed that the dimer forms were more compatible with the XRD analysis results performed for solid-state structures at some molecular geometry parameters. This harmony is more pronounced in the geometry parameters of the -COOH group, which plays a role in the strong hydrogen bonding interaction. In the IR analysis, it was determined that with the effect of hydrogen bond interaction, it shifted to lower frequency values for dimer structures in the high-frequency region, especially in OH and C=O stretch bands and these results were more consistent



Fig. 7. Frequency-conductivity (σ) (S/cm) relationship graph for a) PN1-a and b) PN2 crystal.



Fig. 8. SEM images for a) PN1-a and b) PN2 crystal.

with spectral ones. In the case of the low-frequency region, bending vibrations shifted to high or to low frequencies in some mode assignments in dimer formation of PN structures. The reactivity properties of PN structures were evaluated via the TD-DFT approach, considering the energy band gap and also some global descriptors. PN2 monomer structure has a narrower HOMO-LUMO energy gap, higher global softness, electrophilicity index values, hence it can be said to exhibit a more reactive chemically and a better electrophilic profile compared to PN1. For local reactivity properties of PN structures, Fukui functions and dual descriptors have been examined to provide information about the site selectivity within the molecule toward a nucleophilic or an electrophilic attack. Additionally, MEP and contour maps showed electrophilic and nucleophilic regions of PN1-a and PN2 structures. The potential of using these materials in some industrial applications such as nonlinear optics and electronics has been investigated. PN2 structure, which has a higher heat capacity (65.763 cal.mol⁻¹.K⁻¹ at 298.15 K) and first order hyperpolarizability parameter values $(\beta_{tot}(PN2)/\beta_{tot}(PN1-a)=4.4)$, has a more favorable structure in the thermochemical field and NLO applications than the PN1 structure. When PN1 and PN2 are compared, the conductivity of PN2 is high and it can be thought to be used as an alternative to TiO₂ in dye-based solar cells because charge injection is correlated to the increase in solar cell efficiency.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Gülenay Tunç: Conceptualization, Methodology, Investigation. Betül Canımkurbey: Conceptualization, Methodology, Investigation, Writing - review & editing. Burcu Dedeoğlu: Conceptualization, Methodology, Software, Writing - review & editing. Yunus Zorlu: Conceptualization, Methodology, Investigation, Data curation, Software, Writing - review & editing. Serpil Eryılmaz: Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Project administration. Ayşe Gül Gürek: Conceptualization, Validation, Writing - review & editing, Visualization, Supervision.

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Supplementary materials

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