



A spectroscopic study on new phthalonitrile derivative and its computational background: 4-[(4,5-Diphenyl-4H-1,2,4-triazol-3-yl)sulfanyl]benzene-phthalonitrile



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ABSTRACT

Heterocyclic phthalonitrile derivatives are important precursors in synthesis of new photoactive phthalocyanine compounds. In this study, novel phthalonitrile compound bearing triazole moiety was synthesized and characterized by using spectroscopic techniques such as FT-IR and NMR. The molecular structures of the title compound was analyzed crystallographically and compared with the structural parameters obtained computationally. The orbital energies, electronic absorptions, atomic charge parameters, vibrational frequencies, ground state transitions, ¹H and ¹³C NMR chemical shifts and NBO analysis were computed by using DFT (Density Functional Theory) calculation and compared with the experimental results.

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1. Introduction

Phthalonitriles are excellent precursors for synthesis of phthalocyanine metal complexes having photosensitive properties [1–10]. In addition, phthalonitrile polymers have high thermal resistivity making them a good component in many important technological applications such as composite matrices, adhesives, solar panels and electrical conductors [11–17]. Liquid crystal properties of phthalonitrile derivatives are another important research area [18].

Triazole are an important heterocyclic compound showing medicinal importance respect for pharmacological, insecticidal, fungicidal, and herbicidal, antibacterial, analgesic, anti-inflammatory, antiviral, anti depressant, anti-cancer [19–22]. Anastrozole and Letrozole, 1,2,4-triazole derivatives used treatment of breast cancer [23].

Last decades, computational chemistry has become more important with the latest development in theoretical approaches.

Renewed and advanced calculation methods provide considerable accuracy and low cost computational time in determination of physical and chemical properties of a compound. In light of these developments, one of the aims of computational chemistry is to analyze underlying causes of chemical behaviours of a compound by determining the chemical and physical properties of the compounds.

This study represents synthesis and spectroscopic characterization of a novel triazole substituted phthalonitrile and their investigation of spectroscopic and computational. The title compound was characterized by instrumental techniques such as X-ray crystallography, FT-IR, NMR spectroscopy and mass spectrometry. All computational studies were performed by used the optimized geometry. Theoretical data obtained from computational study, provides better understanding of phthalonitrile derivatives.

2. Experimental and computational details

4,5-diphenyl-4H-1,2,4-triazole-3-thiol (1) was prepared according to literature [24]. The title compound was synthesized from reaction between 4-nitrophthalonitrile (2) and compound (1) in

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DMF at 55 °C. The reaction based on a nucleophilic aromatic substitution and K₂CO₃ was used as basic catalyst. Reaction pathway was shown in Fig. S1. Single crystals, suitable for X-ray analysis were obtained from acetone/petroleum ether solvent system. All theoretical calculations were performed with gaussian 03W software package [25]. All reactions were carried out under dry and oxygen free nitrogen atmosphere using schlenk system. ¹H NMR and APT spectra were recorded on an 400 MHz Agilent NMR spectrometer in CDCl₃. Chemical shifts were reported (δ) relative to Me₄Si as internal standard. IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with ATR technique. FT-IR and NMR spectra were shown in supplementary material (Figs. S2–S4).

2.1. Synthesis of 4-[(4,5-diphenyl-4H-1,2,4-triazol-3-yl)sulfanyl]benzene-phthalonitrile (3)

4,5-diphenyl-4H-1,2,4-triazole-3-thiol (**1**) (0.61 g, 3.2 mmol) and 4-nitrophthalonitrile (**2**) (0.55 g, 3.2 mmol) were dissolved in dry DMF (10 ml) under N₂ atmosphere. After stirring for 10 min at 55 °C, dry fine powdered potassium carbonate (0.48 g, 3.5 mmol) was added portionwise within 2 h with efficient stirring. The reaction mixture was stirred under N₂ atmosphere at 50 °C for 5 days then the mixture was poured into 250 ml ice-water and precipitate was filtered off, washed with water and dried in vacuo. Crude product was purified by column chromatography, in chloroform:methanol solvent system. The single crystals obtained from first fraction in acetone/petroleum ether solvent system. Yield 0.45 g (45%)

IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3071, 2228, 1596, 1582, 1546, 1519, 1492, 1467, 1442, 1429, 1395, 1310, 1285, 1274, 1254, 1214, 1190, 1176, 1156, 1126, 1097, 1070, 1045, 1024, 1008, 972, 917, 894, 863, 837, 767, 693, 686

¹H NMR (DMSO), (δ: ppm): 7.2 (d, 2H), 7.28–7.36 (m, 2H), 7.38–7.62 (m, 6H), 7.64–7.74 (m, 3H)

APT (CDCl₃), (δ: ppm): 114.23 (C), 114.70 (C), 115.10 (C), 116.73 (C), 125.90(C), 127.48 (CH), 128.50 (CH), 128.89 (CH), 130.30 (CH), 130.67 (CH), 133.27 (CH), 133.40 (CH), 133.84 (C), 133.97, 140.54 (C), 146.74 (C), 156.66 (C)

2.2. Crystal structure of the compound (3)

The X-ray diffraction data for the crystal of compound (**3**) were collected using a Bruker Smart CCD diffractometer. The X-ray source was CuK α ($\lambda = 1.54178 \text{ \AA}$). APEX2 [26] and Bruker SAINT [26] software were used during collecting data and refining cell, respectively. We also used ORTEP III [27] and WinGX software [28] programs to construct figures and to prepare manuscript for publishing. The programs used for solving and refining the molecular structure were SELXS-97 [29], SHELXL-97 [29]. Crystallographic data were deposited in CSD under CCDC registration number 1456742. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

2.3. Computational details

The geometric optimization and frequency calculation of the title compound was performed by DFT calculations with a hybrid functional B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) [30,31] and 6-31G(d) was chosen as basis set. All theoretical studies were conducted by Gaussian 03W software package [23,25]. Geometric optimization of the

compound was conducted DFT/B3LYP/6-31G(d) by used crystallographic geometrical parameters. For the DFT study, the harmonic vibrational frequencies were calculated at the same level of theory with optimization study and obtained vibrational frequency scaled by 0.9614 [23]. Absence of the imaginary frequency indicated that the structure was in stationary point. All assignments and molecular screenings were made using Gauss-view molecular visualisation program [32]. Time-dependent density functional theory (TD-DFT) was used to calculate the electronic absorption properties with hybrid functional with 6-31 G (d,p)++ basis set for 50 singlet transitions. ¹H and ¹³C chemical shift calculations were studied at B3LYP/6311++G(2d,p) basis set with GIAO (Gauge-Independent Atomic Orbital). IEF-PCM method was used as solvation model and chloroform was determined as solvent [33–35]. NBO calculations were performed by using NBO 3.1 in Gaussian 03W software package [36].

3. Results and discussion

3.1. Description of the crystal structure of the title compound

The molecular structure has two phenyl rings substituted on C5 and N4 atoms and a (sulfanyl) benzene-phthalonitrile moiety substituted on C3 atom. The N–N [1.382(5) Å] bond length agree with the values given bond lengths for similar structures in the literature {N1–N2 = 1.393(3) Å [37], N3–N4 = 1.399(4) Å [38], N3–N4 = 1.384(3) Å [39], N1–N2 = 1.372(2) Å [40] and N1–N3 = 1.379(6) Å [41]}. An increase can be seen in this type of bond lengths since substitute groups cause stretching on the N–N bond length in the molecules that has substituted groups on position 1 and position 2 in the 1,2,4-triazole ring. The N3–N4 = 1.404(4) Å in the literature [42] shows this type of stretching interaction. All other crystallographic parameters are listed in Table 1 and computational structural parameters were compared with crystallographic ones in Table 2. The crystal structure and unit cell of compound 3 were shown in Fig. 1 and Fig. 2.

Three phenyl rings (A: C31–C36, B: C41–C46 and C: C51–C56) and a 1,2,4-triazole ring (D: N1, N2, C3, N4, C5) on the molecule have planar conformation. The dihedral angles between these rings, A–B, A–C, A–D, B–C, B–D and C–D are 52.12(1), 74.00(2), 85.72(1), 63.37(2), 64.71(2) and 32.38(2)°; respectively.

Crystal structure of the title compound involves an intramolecular hydrogen bond, an intermolecular hydrogen bond and a C–H ... π type interaction. All details about available hydrogen bonds are given in Table 3 and Fig. 3. This C–H ... π type contact involves ring B of symmetry related molecule at (x, -1+y, z) [C33–H33 ... Cg; C33 ... Cg = 3.601(5) Å, H33 ... Cg = 2.90 Å and C33–H33 ... Cg = 133°; Cg is the centroid of ring B at (x, -1+y,z)]

3.2. Assignments of the vibrational modes of the compound

The title compound composes of 41 atoms and has 117 normal vibrational modes. In this study, all vibrational modes analyzed and some important of them were assignment in Table 4. In computational studies, raw vibrational frequencies generally have larger value than experimental ones. The reason for this is the differences of theoretical and experimental methods and the nature of quantum chemical approximations. The theoretical calculations are performed for a single molecule in vacuum media whereas experimental IR spectrum is recorded in solid or liquid phase. Vibrational data of compound (**3**) obtained from computational study were compared with the experimental IR spectrum. Due to systematic errors that occurred in frequency calculation, scaling factor value was taken as 0.9614 [43]. Some theoretical and experimental vibrational data were shown in Table 4. The calculated vibrational

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