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Crystal Structure of 5-Nitro-4-(4-methoxyphenoxy)phthalonitrile

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Abstract: This article presents findings on the synthesis and crystal structure analysis of 5-nitro-4-(4-methoxyphenoxy)phthalonitrile. The crystal structure was meticulously refined using X-ray diffraction techniques, which allowed for a detailed examination of the molecular arrangement within the crystal. The manuscript elaborates on the significant intermolecular and intramolecular interactions that contribute to the overall crystal packing, highlighting how these interactions influence the stability and properties of the material.

Keywords: phthalonitrile; X-ray diffraction; methoxy groups

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1. Introduction

Substituted phthalonitriles have been extensively studied by researchers over the past century [1–4]. This interest is attributed to their potential applications as high-conductivity resins [5,6], in electrical engineering [7], and as key components for the production of pigments and thermally stable composite materials [8,9]. The characteristics of crystalline packing play a crucial role in the physicochemical properties exhibited by these compounds. Therefore, elucidating the influence of various substituents is one of the primary factors for the successful design of high-performance molecular structures that meet contemporary technological demands.

Previously, we investigated the crystalline structures of methoxyphenoxy-substituted phthalonitriles with *m*-, *o*-, and *p*-substitutions of the methoxy group [10,11]. It was demonstrated that the position of the substituent significantly affects the crystalline packing of the structures, which, in turn, directly influences the physicochemical properties of the compounds. This work presents the results of an analysis of a structurally modified version of the studied methoxyphenoxynitriles [10,11]. A nitro group was introduced at the 5-position of the nitrile molecule, which, as described in the literature, contributes substantial changes to the properties exhibited by the structures.

2. Results and Discussion

The analyzed 5-nitro-4-(4-methoxyphenoxy)phthalonitrile was found to crystallize as a solvent-free crystal, whose structure is illustrated in Figure 1. The phthalonitrile and phenoxy-rings are oriented at a dihedral angle equal to 89°. The methoxy group is positioned nearly in the plane of the phenoxy group. The deviation of the carbon atom from the plane of the aromatic ring is measured at 0.17 Å. The nitro group is rotated relative to the plane of the phthalonitrile, with the corresponding dihedral angle measuring 27.9°. The C-N bond distances are 1.133(2) Å and 1.136(2) Å, while the N-O distances in the nitro group are not significantly different, measuring 1.210(2) Å and 1.219(2) Å. In addition, the structure is stabilized by the presence of an intramolecular interaction (2.618(2) Å) between the spacer oxygen atom of the bridging group and the oxygen atom of the nitro group O1···O3 (Figure 2a). It should be noted that this distance is significantly shorter than the sum of the van der Waals radii of two oxygen atoms (3.1 Å) [12]. Overall, the primary geometric characteristics are in excellent agreement with previously published related compounds [13–15].

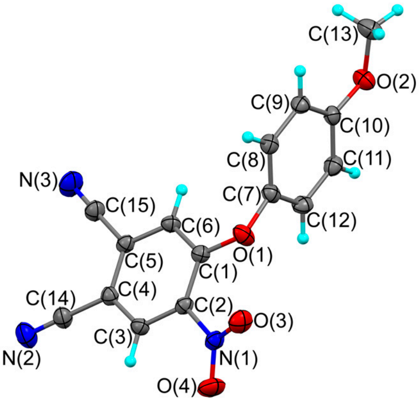


Figure 1. The molecular structure of 5-nitro-4-(4-methoxyphenoxy)phthalonitrile, shown with atom labeling. Displacement ellipsoids are drawn at the 25% probability level.

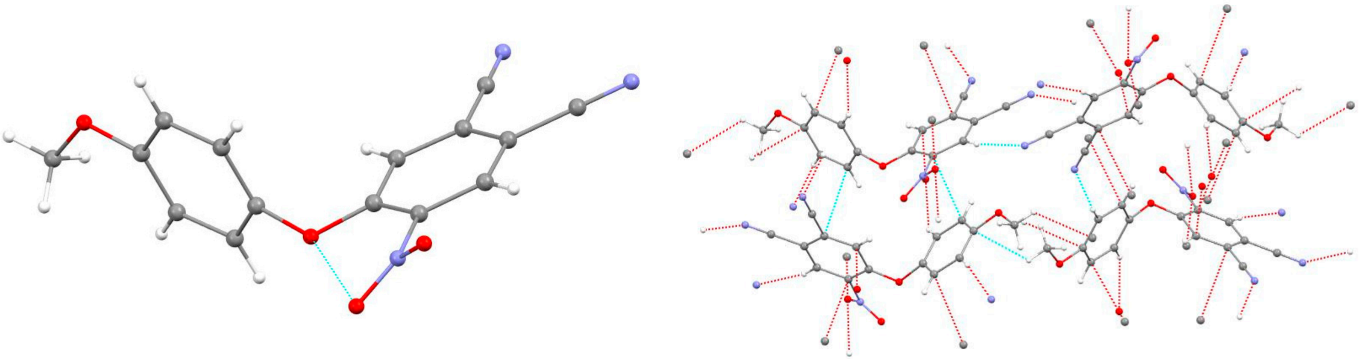

(**a**) (**b**)

Figure 2. The molecular structure and the system of (**a**) intra- and (**b**) intermolecular interactions for 5-nitro-4-(4-methoxyphenoxy)phthalonitrile.

The main structure-forming motifs in the crystal include the implementation of the short intermolecular interactions C14-N2···H3A and C15-N3···H9A, which are carried out through the cyano groups of the phthalonitrile fragment, as well as the O2···O3, O2···O4, and O1···O4 interactions involving the oxygen atoms of the nitro group (Figure 2b). The nitro group also takes part in the realization of one C-H···O van der Waals contact in the crystal (Table 1).

Table 1. Short interaction geometry parameters (Å, °) for 5-nitro-4-(4-methoxyphenoxy)phthalonitrile.

D–H···A/D···A	D–H	H···A	D···A	D–H···A
O1···O3	N/A	N/A	2.618(2)	N/A
C3-H3A···N2 ^{i,*}	0.93	2.69	3.600(3)	166.8
C9-H9A···N3 ^{ii}	0.93	2.64	3.550(2)	165.2
C12-H12A···O4 ^{iii}	0.93	2.51	3.276(2)	140.0
C2···C11 ^{iv}	N/A	N/A	3.627(2)	N/A
C5···C8 ^{v}	N/A	N/A	3.352(2)	N/A
O2···O3 ^{v}	N/A	N/A	3.999(2)	N/A
O2···O4 ^{v}	N/A	N/A	3.752(3)	N/A
O1···O4 ^{vi}	N/A	N/A	3.773(2)	N/A

* Symmetry code: (^{i}): x − 1/2, −y + 3/2, −z + 1; (^{ii}): −x + 2, y − 1/2, −z + 1/2; (^{iii}): −x, y + 1/2, −z + 1/2; (^{iv}): 1 − x, y − 1/2, −z + 1/2; (^{v}): 1 − x, 1/2 + y, 1/2 − z; (^{vi}): 1 + x, y, z.

In addition, the presence of a nitro group in the structure, oriented with respect to the plane of phthalodinitrile, resulted in an increased distance between the planes of the aromatic systems. This distortion results in an inability to achieve significant π-stacking interactions between aromatic fragments during packing. Consequently, only isolated "head-to-tail"-type overlaps of p-orbitals between aromatic fragments are observed for atoms C5···C8 and C2···C11 (Figure 2b). The crystal packing system is illustrated in Figure 3. The distance between the bond center N(3)≡C(15) and the center of the aromatic ring of a neighboring molecule is 3.77 Å, while the distance between the center of the nitro group and the center of the aromatic ring of another molecule is 3.78 Å. These geometric characteristics may indicate the presence of intermolecular π. . .π interactions in the crystal, as the geometric criterion for such contacts ranges from 3.3 to 3.8 Å [16].

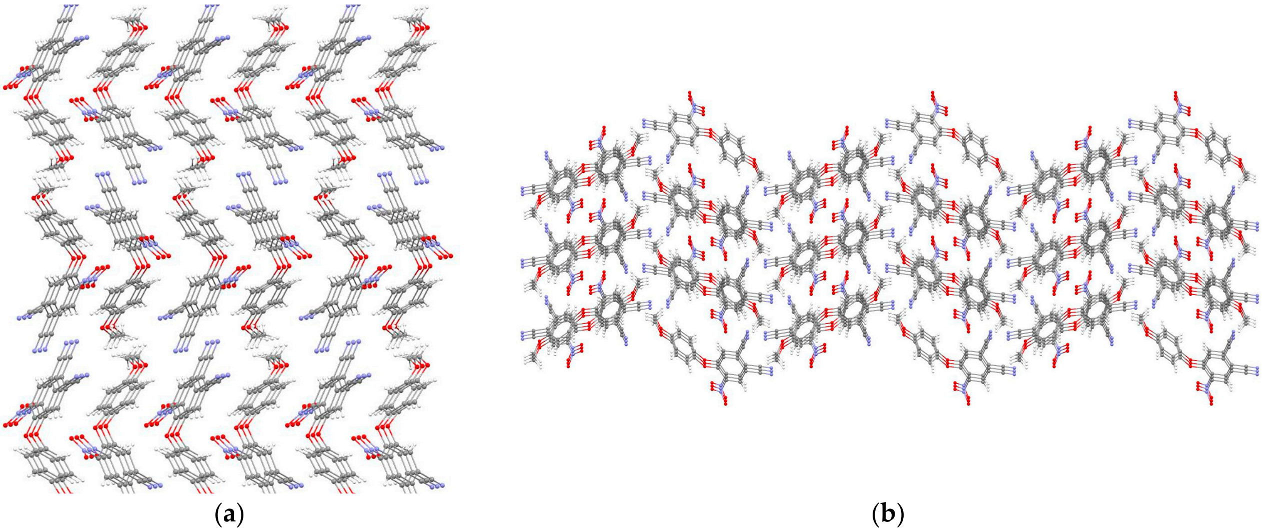
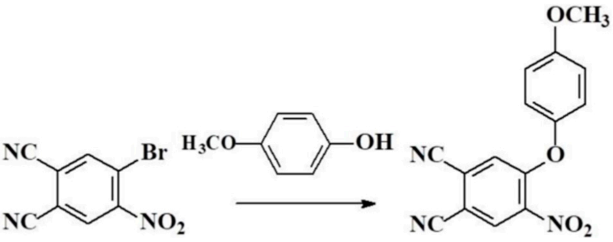

(**a**) (**b**)

Figure 3. A view along the (**a**) and (**b**) axes of the crystal packing of 5-nitro-4-(4-methoxyphenoxy) phthalonitrile. Intermolecular hydrogen bonds have been removed for clarity.

3. Materials and Methods

3.1. Synthesis of 5-Nitro-4-(4-methoxyphenoxy)phthalonitrile

A solution of 0.8 g (0.0032 mol) of 4-bromo-5-nitrophthalonitrile and 0.4 g (0.0032 mol) of 4-methoxyphenol was prepared in 10 mL of dimethylformamide (DMF) (Scheme 1). To the resulting solution, a solution containing 1.3 g (0.0094 mol) of potassium carbonate (K_2CO_3) in 3.3 mL of water was added, and the mixture was stirred at 30 °C for a duration of 1.5 h (Scheme 1). The resultant precipitate was filtered, washed with water, recrystallized from DMF, and subsequently dried in air at 75 °C. Yield: 0.72 g (75%). Found, %: C—60.6, H—3.2, N = 14.1, $C_{15}H_9N_3O_4$; calculated—C—61.0, H—3.1, N—14.2. MALDI-TOF MS, m/z: found—295 [M] (Figure S1), calculated—295.25. FT-IR, υ, cm^{-1}: 2237 (CN), 1249 (Ar-O-Ar), 1481 (N=O), 1281 (C-O-C_v) (Figure S2). ^1H NMR, δ, ppm (500 MHz, Acetone-d_6): 8.74 (s, 1H), 7.73 (s, 1H), 7.26 (d, J = 8.9 Hz, 2H), 7.11 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H) (Figure S3). ^{13}C NMR (125 MHz, Acetone-d_6): 158.26; 154.86; 146.44; 142.09; 131.06; 123.22; 121.82; 120.46; 115.70; 114.19; 114.03; 108.80; 55.18 (Figure S4).



Scheme 1. General pathway of 5-nitro-4-(4-methoxyphenoxy)phthalonitrile synthesis.

3.2. X-Ray Crystallography

The diffraction data for 5-nitro-4-(4-methoxyphenoxy)phthalonitrile were collected on an Oxford Excalibur Eos diffractometer (Mo-Kα radiation, ω-scan technique, λ = 0.71073 Å, Agilent, Polish, Varshava). The intensity data were integrated by the CrysAlisPro program (Agilent, Polish, Varshava) [17]. The structure was solved by the dual method [18] and was refined on F^2_{hkl} using the SHELXTL package (Sheldrik) [19]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined using the riding model (U_{iso}(H) = 1.5 U_{eq}(C) for the CH_3 group and U_{iso}(H) = 1.2 U_{eq}(C) for other groups). The CrysAlisPro program was used to perform absorption corrections.

A yellow prism-shaped single crystal (0.71 × 0.66 × 0.39 mm) was selected for SC-XRD analysis. The crystal data for 5-nitro-4-(4-methoxyphenoxy)phthalonitrile were as follows: orthorhombic crystal system, space group $P2_12_12_1$, unit cell dimensions: a = 6.66446(13) Å, b = 9.38249(18) Å, c = 22.3970(6) Å, V = 1400.47(5) Å^3, Z = 4, d_{calc} = 1.400 g/cm^3, μ = 0.105 mm^{-1}, F(000) = 608, reflection collected/unique = 12310/4079, R_{int} = 0.0159, S = 1.031, R_1 = 0.0339 and wR_2 = 0.0929 [$I > 2\sigma(I)$], R_1 = 0.0378 and wR_2 = 0.0964 (all data), largest diff. peak and hole 0.174 and −0.167 $e \cdot Å^{-3}$.

4. Conclusions

The data on the crystalline packing of 5-nitro-4-(4-methoxyphenoxy)phthalonitrile reveal that the structure is primarily stabilized by a significant number of short intermolecular interactions, which arise due to the presence of heteroatom fragments in the molecule. The most substantial contributions to the stabilization of the packing come from intermolecular interactions between the nitrogen atoms of the nitrile group and the hydrogen atoms of the aromatic ring in the phthalonitrile fragment, as well as between the oxygen atom of the nitro group and the hydrogen atom of the aromatic ring in the phenoxy substituent. Additionally, interactions of the oxygen–oxygen type between the oxygen atoms of the nitro, methoxy, and phenoxy groups also play a crucial role in stabilizing the structure.

Supplementary Materials: CCDC 2407616 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures (accessed on 4 December 2024). Figure S1: MALDI-TOF mass spectrum for 5-nitro-4-(4-methoxyphenoxy)phthalonitrile; Figure S2: FT-IR spectrum for 5-nitro-4-(4-methoxyphenoxy)phthalonitrile; Figure S3: ^{1}H NMR spectrum for 5-nitro-4-(4-methoxyphenoxy)phthalonitrile; Figure S4: ^{13}C NMR spectrum for 5-nitro-4-(4-methoxyphenoxy)phthalonitrile.

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Data Availability Statement: Data available on request.

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Conflicts of Interest: The authors declare no conflicts of interest.

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