



Synthesis and Crystal Structure of 4-(2-Isopropyl-5-methylcyclohexyloxy)phthalonitrile

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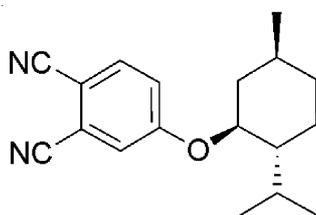
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A chiral phthalonitrile compound has been prepared by the reaction of chiral menthol (2-isopropyl-5-methylcyclohexanol) and 4-nitrophthalonitrile with potassium carbonate and DMF at 40 °C. Its crystal structure was determined by single-crystal X-ray diffraction. The crystal belongs to the orthorhombic system, space group P 2₁ 2₁ 2₁ with a = 6.9073(16) Å, b = 8.0803(19) Å, c = 30.558(8) Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $M_r = 282.38$, $V = 11705.5(7) \text{ \AA}^3$, $Z = 4$, $D_c = 1.100 \text{ g/cm}^3$, $F_{(000)} = 608$, $\mu = 0.069 \text{ mm}^{-1}$, $R = 0.0690$ and $wR = 0.1642$ for 1535 observed reflections ($I > 2\sigma(I)$). In the structure, $\pi \dots \pi$ stacking interactions among phthalonitrile rings make the molecule more stable and the cyclohexane ring adopts a chair conformation.

Key Words: Synthesis, Crystal structure, Phthalonitrile, Cyclohexane.

INTRODUCTION

As an important organic intermediate, phthalocyanines have been extensively studied over the past century because of their potential applications in dyes and pigments, optical data storage, catalysis, non-linear optics (NLO), photodynamic therapy agents, corrosion inhibitors¹⁻⁴. Also, a large number of phthalocyanine derivatives have been extensively used to construct molecular-based electronic and optical devices and liquid-crystalline materials, such as electronic wires, switches, electroluminescence devices, field-effect transistors and photovoltaic devices⁵⁻⁸. Recently, phthalocyanine derivatives with chiral substituents have emerged increasing interest due to their potential use for biological and optoelectronic applications^{9,10}. For this purpose, a large number of chiral phthalocyanine compounds have been synthesized. Herein, we report the synthesis and crystal structure of the title compound *i.e.*, [4-(2-isopropyl-5-methylcyclohexyloxy)phthalonitrile] which is a typical phthalonitrile compound containing chiral unit (**Scheme-I**).



Scheme-I

EXPERIMENTAL

All the reagents and solvents from commercial sources were used without further purification.

Potassium carbonate (960 mg, 6.96 mmol), 4-nitrophthalonitrile (500 mg, 2.89 mmol) and 2-isopropyl-5-methylcyclohexanol (903 mg, 5.78 mmol) were added into DMF (15 mL) and stirred at 40 °C for 4 days under a nitrogen atmosphere. Then the reaction mixture was poured into ice water (100 mL) and the aqueous layer was extracted with ethyl acetate. After being dried over anhydrous MgSO_4 , the organic layer was evaporated and the residue was purified by silica gel chromatography with 1:6 (v/v) ethyl acetate/petroleum ether (60-90 °C) as eluent and yielded a yellowish solid (65 %, yield).

Data collection and structure determination: A single crystal of the title compound with dimensions of 0.13 mm \times 0.11 mm \times 0.19 mm was selected for X-ray diffraction. The diffraction data were collected with a SMART CCD diffractometer equipped with a graphite-monochromatic $\text{MoK}\alpha$ ($\lambda = 0.071073 \text{ nm}$) radiation using an ω scan mode at 293(2) K. In the range of $2.67 < \theta < 24.84^\circ$, a total of 8211 reflections were collected and 2934 were independent ($R_{\text{int}} = 0.0626$), of which 1535 were observed.

The structure of the title compound was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXS-97 and SHELXL-97 programs¹¹. All non-hydrogen atoms were refined by full-matrix least-squares

method, while all hydrogen atoms were placed in the geometrically calculated positions. The contributions of hydrogen atoms were included in the structure-factor calculations. The atomic scattering factors and anomalous dispersion corrections were taken from International table for X-ray crystallography¹². The final cycle of refinement gave $R = 0.0690$, $wR = 0.1642$ ($w = 1/[\sigma^2(F_o^2) + (0.0956P)^2 + 0.000P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.009$, $(\Delta/\sigma)_{\max} = 0.000$, $(\Delta\rho)_{\min} = -0.172$ and $(\Delta\rho)_{\max} = 0.178 \text{ e}/\text{\AA}^3$. The crystal and experimental data are given in Table-1.

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR THE TITLE COMPOUND

Empirical formula	$C_{18}H_{22}N_2O$
Formula weight	282.38
Temperature (K)	293(2)
Wavelength (\AA)	0.71073
Crystal system	Orthorhombic
Space group	$P 2_1 2_1 2_1$
Unit cell dimensions	$a = 6.9073(16) \text{\AA}$ $\alpha = 90^\circ$ $b = 8.0803(19) \text{\AA}$ $\beta = 90^\circ$ $c = 30.558(8) \text{\AA}$ $\gamma = 90^\circ$
Volume (\AA^3), Z	1705.5(7), 4
Calculated density (g/cm^3)	1.100
Absorption coefficient (mm^{-1})	0.069
$F(000)$	552
Crystal size (mm)	0.13 mm \times 0.11 mm \times 0.09 mm
Theta range for data collection ($^\circ$)	2.67-24.84
Limiting indices	$-8 \leq h \leq 7$, $-9 \leq k \leq 9$, $-36 \leq l \leq 33$
Reflections collected/unique	8211/2934 [$R_{\text{int}} = 0.0626$]
Completeness to theta = 24.84	99.5 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2934/0/193
Goodness-of-fit on F^2	1.009
Final R indices [$I > 2\sigma(I)$] R indices (all data)	$R_1 = 0.0690$, $wR_2 = 0.1642$ $R_1 = 0.1367$, $wR_2 = 0.1965$
Largest diff. peak and hole ($\text{Einstein } \text{\AA}^{-3}$)	0.178 and -0.172

RESULTS AND DISCUSSION

The selected bond distances and bond angles are given in Table-2. A displacement ellipsoid plot of with atomic numbering scheme and a perspective view of the crystal in a unit cell are shown in Figs. 1 and 2, respectively.

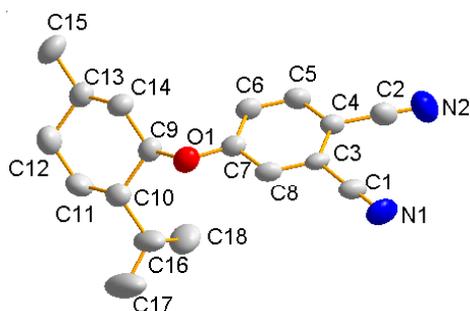


Fig. 1. Molecular structure for the title compound with atomic numbering scheme

In the title compound, the bond lengths and angles in the phenyl ring are generally normal. As can be seen from the

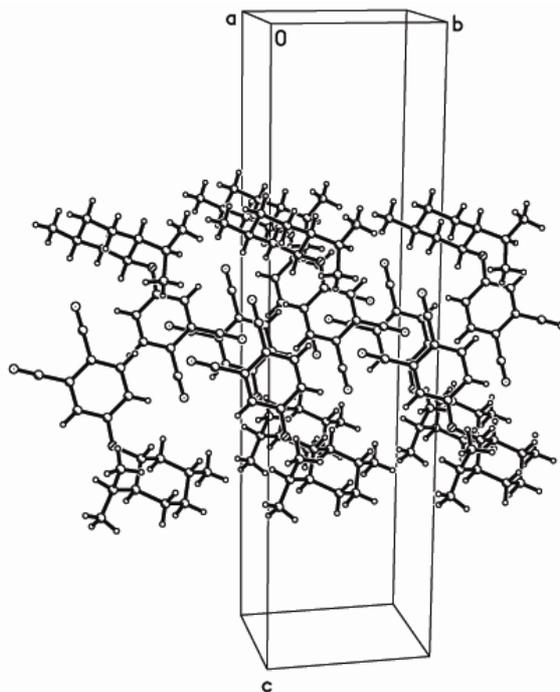


Fig. 2. View of crystal packing down the b axis for the title compound

TABLE-2
SELECTED BOND LENGTHS (\AA) AND BOND ANGLES ($^\circ$)

Bond	Dist.	Bond	Dist.
O(1)-C(7)	1.349(4)	C(9)-C(14)	1.494(5)
O(1)-C(9)	1.464(5)	C(9)-C(10)	1.522(6)
N(1)-C(1)	1.145(5)	C(4)-C(5)	1.380(6)
N(2)-C(2)	1.138(6)	C(10)-C(11)	1.522(7)
C(1)-C(3)	1.437(6)	C(10)-C(16)	1.536(7)
C(2)-C(4)	1.440(7)	C(11)-C(12)	1.520(7)
C(3)-C(8)	1.372(5)	C(12)-C(13)	1.528(7)
C(3)-C(4)	1.388(5)	C(13)-C(14)	1.506(6)
C(4)-C(5)	1.380(6)	C(13)-C(15)	1.519(7)
C(5)-C(6)	1.367(5)	C(16)-C(17)	1.388(8)
C(6)-C(7)	1.372(5)	C(16)-C(18)	1.502(7)
Angle	($^\circ$)	Angle	($^\circ$)
C(7)-O(1)-C(9)	119.8(3)	C(3)-C(8)-C(7)	119.9(3)
N(1)-C(1)-C(3)	177.4(6)	O(1)-C(9)-C(14)	110.7(4)
N(2)-C(2)-C(4)	178.8(5)	O(1)-C(9)-C(10)	106.2(3)
C(8)-C(3)-C(4)	120.5(4)	C(14)-C(9)-C(10)	112.8(3)
C(8)-C(3)-C(1)	119.1(3)	C(9)-C(10)-C(11)	106.8(4)
C(4)-C(3)-C(1)	120.4(4)	C(9)-C(10)-C(16)	112.0(4)
C(5)-C(4)-C(3)	118.9(4)	C(11)-C(10)-C(16)	115.9(5)
C(5)-C(4)-C(2)	120.6(4)	C(12)-C(11)-C(10)	112.2(4)
C(3)-C(4)-C(2)	120.4(4)	C(11)-C(12)-C(13)	111.8(4)
C(6)-C(5)-C(4)	120.7(4)	C(14)-C(13)-C(15)	111.8(4)
C(5)-C(6)-C(7)	120.7(4)	C(14)-C(13)-C(12)	108.8(4)
O(1)-C(7)-C(6)	125.2(4)	C(15)-C(13)-C(12)	112.5(4)
O(1)-C(7)-C(8)	115.6(3)	C(9)-C(14)-C(13)	112.2(4)
C(6)-C(7)-C(8)	119.2(4)	C(17)-C(16)-C(18)	115.9(5)
C(17)-C(16)-C(10)	115.9(5)	C(18)-C(16)-C(10)	115.7(4)

crystal structure (Fig. 1), the central O(1) atom is bridged by a phthalonitrile ring *via* a C-O double bond (O(1)-C(7) 1.349(4) \AA) and cyclohexane ring *via* the single O(1)-C(9) bond (1.464(5) \AA), forming the C(7)-O(1)-C(9) bond angle of 119.8(3) $^\circ$. In phthalonitrile ring, the triple bond lengths of $C1 \equiv N1$ (1.145(5), \AA) and $C2 \equiv N2$ (1.138(6) \AA) are agreement with those of the similar structures [$C \equiv N$, 1.140(2) \AA

TABLE-3
 INTERMOLECULAR INTERACTION DISTANCES (Å)

D-H...A	Symmetry	D-H	H...A	D...A	D-H...A (°)
C(16)-H(16)...O(1)		0.98	2.33	2.806(7)	109.18

 TABLE-4
 $\pi \cdots \pi$ STACKING INTERACTIONS

Ring	Symmetry	Centroid-to centroid distance (Å)	Perpendicular distance of Cg(I) on ring J (Å)	Perpendicular distance of Cg(J) on ring I (Å)	Dihedral angle between planes I and J (°)
Cg(1)...Cg(1)	-1/2 + x, 3/2 -y, 2-z	5.375	3.351	3.536	8.92
Cg(1)...Cg(1)	1/2 + X, 3/2 -Y, 2-Z	5.375	3.536	3.350	8.92
Cg(1): C(3) > C(4) > C(5) > C(6) > C(7) > C(8).					

and 1.142(2) Å]¹³. The bond angles of N1-C1-C3 (177.4(6)°) and N2-C2-C4 (178.8(5)°) are also consistent with values found for the similar compounds [172.2(2) and 178.6(2)°]¹³. It is noteworthy that the cyclohexane ring exhibits a chair-like configuration, with puckering parameters¹⁴ for Q = 0.577(5) Å, q₂ = 0.023(5) Å, q₃ = -0.576(5) Å, J = 177.6(5)°, J = 235(13)°. The four atoms of C(9) atom, C(10) and C(11) in cyclohexane ring with conjunction oxygen atom O(1) are fairly planar (plane equation: 0.7674x - 0.133y + 0.627z = 16.04) and the largest deviation is 0.006 Å. The phthalonitrile ring with the conjunction oxygen atom O(1) is also quite planar (plane equation: 0.9980x - 0.0459y + 0.0440z = 0.74) and the largest deviation is 0.043 Å. The dihedral angle between those two planes is 36.9(3)°.

In addition, there are classical C(16)-H(16)...O(1) intramolecular hydrogen bonds (Table-3). In the mean time, there are two types of $\pi \cdots \pi$ stacking interactions in the packing diagram, with a centroid-centroid separation of 5.375 Å (Table-4). In solid state, all above extensive hydrogen bond stabilize the crystal structure. However, there exists no intermolecular hydrogen bonds in the lattice (Fig. 2).

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REFERENCES

1. N. Nombona, E. Antunes and T. Nyokong, *Dyes Pigm.*, **86**, 68 (2010).
2. N. Kobayashi, *Coord. Chem. Rev.*, **219**, 99 (2001).
3. K. Suda, S Nakajima, Y. Satoh and T. Takanami, *Chem. Commun.*, 1255 (2009).
4. E.A. LukCentyanets, *J. Porphyrins Phthalocyanines*, **3**, 424 (1999).
5. L. Brunsveld, H. Zhang, M. Glasbeek and J.A.J.M. Vekemans, *J. Am. Chem. Soc.*, **122**, 6175 (2000).
6. J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia and R.H. Friend, *Nature*, **376**, 498 (1995).
7. J.M. Rivera, T. Martin and J. Rebek Jr., *Science*, **279**, 1021 (1998).
8. M. Kimura, H. Ueki and K. Ohta, *Langmuir*, **22**, 5051 (2006).
9. K. Adachi, K. Chayama and H. Watarai, *Langmuir*, **22**, 1630 (2006).
10. K. Adachi, K. Chayama and H. Watarai, *Chirality*, **18**, 599 (2006).
11. G.M. Sheldrick, *Acta Cryst.*, **A64**, 112 (2008).
12. Siemens, Area Detector Control and Integration Software, USA (1996).
13. L. Yu, X. Zhou, Y. Yin, R. Li and T. Peng, *Acta Cryst.*, **E66**, o2527 (2010).
14. D. Cremer and J.A. Pople, *J. Am. Chem. Soc.*, **97**, 1354 (1975).