SYNTHESIS AND CRYSTALLOGRAPHIC STRUCTURE ANALYSIS OF 4,4'-OXYDIANILINE

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ABSTRACT

The title compound, 4,4'-Oxydianiline, was synthesized in good yield by the reaction of 4-fluoro nitrobenzene with 4-nitrophenol in dimethylacetamide (DMAc) and toluene at 165 °C for 4 h in the presence of K₂CO₃ to obtain 4,4'-dinitrodiphenyl ether, which was then treated with Pd/C in N, N-dimethyl formamide (DMF) at 65 °C for 12 h. The crude product was recrystallized and elucidated by spectroscopic techniques (H NMR, LC-MS), elemental analyses. The compound crystallizes in the orthorhombic crystal system with space group P2₁2₁2₁ with unit cell parameters: a = 5.7203(10) Å, b = 7.7326(14) Å, c = 22.8219(42) Å and Z = 4. The crystal structure has been solved by using direct methods and refined by full-matrix least squares procedures to a final R-factor of 0.028 for 1835 observed reflections. The structure exhibits intermolecular H-bonds of the type N–H...O and N–H...N. N–H... π interactions are also observed in the structure.

Keywords: X-ray Diffraction, Direct Methods, Intermolecular interactions, Crystal, Synthesis.

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INTRODUCTION

The use of aromatic amines in the production of polyimide films has led to the development of different materials with great potential for commercial applications such as lightweight batteries, light-emitting diodes¹, capacitors², electrochromic devices^{3,4} and optoelectronic devices⁵, and high temperature resistant products.^{6,7} Conducting ODA polymer films have found application in the field of bio-sensors and bio-electrochemistry.^{8,9} Polyaromatic compounds have been reported to show high biological activity, for example polyaromatic hydrocarbons are considered to be one of the robust antitumor agents.¹⁰⁻¹² In view of its wide range of biological properties and as part of our ongoing work¹³⁻¹⁵ the synthesis and characterization of the title compound was carried out.

EXPERIMENTAL

General

All solvents and reagents were purchased from Sigma Aldrich Chemicals Pvt Ltd. TLC was performed on aluminum-backed silica plates and visualized by UV-light. Melting points were determined on an electrically heated VMP-III apparatus. The elemental analyses of the compounds were performed on a Perkin Elmer 2400 elemental analyzer. The ¹H NMR spectra were recorded on VNMRs-400 Agilent-NMR spectrophotometer in DMSO. Chemical shifts are given in parts per million downfield from tetramethylsilane.

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The mass spectra were obtained with a VG70-70H spectrophotometer and the elemental analysis (C, H) was performed on Elementar Vario EL III elemental analyzer. The results of elemental analyses are within $\pm 0.5\%$ value.

Synthetic Procedure for 4,4'-Dinitrodiphenyl Ether (3)

In a round-bottomed flask containing a mixture of 4-fluoro nitrobenzene (1, 10.7 g, 49.3 mmol), 4-nitrophenol (2, 6.85 g, 49.3 mmol), (6.80 g, 49.3 mmol) of potassium carbonate, 150 mL of dimethylacetamide (DMAc) and 25 mL of toluene was stirred at 130 °C for 2 h. The temperature of the reaction was then raised to 165 °C, and the mixture was stirred at this temperature for 4 h. The reaction mixture was cooled to 85 °C, and the solvent under reduced pressure of 15-25 torr was evaporated. The residue was washed with 200 mL of water and the compound (3) was obtained by recrystallization from acetic acid.

Synthetic Procedure for 4,4'-Diaminodiphenyl Ether (4)

A mixture of (3, 10.50 g, 31.2 mmol) and (0.3 g, 10%) of Pd/C in 150 mL of *N,N*-dimethyl formamide (DMF) was stirred at 65 °C for 12 h under hydrogen atmosphere. The Pd/C was then removed by filtration; the solvent was evaporated under reduced pressure of 15-20 torr and the title compound (4) was then obtained by distillation under reduced pressure as shown in Fig.-1. Schematic of H NMR and LC-MS spectra are shown in Fig.-2 and 3, respectively.

Fig.-1: Schematic Representation of The Synthesis of The Title Compound (4).

Spectral Data for 4,4'-dinitrodiphenyl ether (3)

Yield 80%; M.P. 140-145 °C; 1H NMR (400 MHz, DMSO- d_6) δ (ppm): 7.21-8.27 (m, 8H, Ar-H); LC-MS m/z : 261 [M+1]. Anal. Calcd. for $C_{12}H_8N_2O_5$ (260): C, 55.39; H, 3.10; N, 10.77. Found: C, 55.31; H, 3.04; N, 10.70%.

Spectral Data for 4,4'-oxydianiline (4)

Yield 85%; M.P. 187 -191 °C; 1H NMR (400 MHz, DMSO- d_6) δ (ppm): 4.75 (s, 4H, 2NH $_2$), 6.49-6.63 (m, 8H, Ar-H); LC-MS m/z : 201 [M+1]. Anal. Calcd. for $C_{12}H_{12}N_2O$ (200): C, 71.98; H, 6.04; N, 13.99. Found: C, 71.88; H, 6.00; N, 13.89 %.

X-ray Intensity Data Collection, Structure Solution And Structure Refinement

X-ray intensity data of the crystal of dimensions 0.30 X 0.20 X 0.10 mm³ were collected on *Bruker APEX2* CCD area-detector diffractometer¹⁶ equipped with graphite monochromated MoK α radiation (λ = 0.710 Å). X-ray intensity data of 12684 reflections were collected at 293(2) K and out of these reflections 1964 were found unique. The intensities were measured by ω scan mode for θ ranges 1.79° to 26°. 1835 reflections with $I > 2\sigma(I)$ were treated as observed. Data were corrected for Lorentz-polarization and absorption factors. The structure was solved by direct methods using SHELXS97¹⁷ and was refined using SHELXL97.¹⁷ All non-hydrogen atoms of the molecule were located from the best E-map. All the

hydrogen atoms were geometrically fixed (except N1 and N2 hydrogen atoms) and allowed to ride on their parent carbon atoms with C-H = 0.93-0.97 Å.

Fig.-2: ¹H NMR Spectrum of Compound (4).

Fig.-3: LC-MS Spectrum of Compound (4).

The final refinement cycles converged to an R-factor of 0.028 and $wR(F^2) = 0.075$ for 1835 observed reflections. Residual electron densities range from -0.13 to 0.13 $e\text{\AA}^{-3}$. Atomic scattering factors were

taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables- 4.2.6.8 and 6.1.1.4). The Geometry of the molecule was calculated using the WinGX¹⁸, PARST¹⁹ and PLATON²⁰ software. The crystallographic information file (CIF) has been deposited at the Cambridge Crystallographic Data Centre and the structure-refinement data is presented in Table-1.

Table-1: Crystallographic Characteristic and Structure-Refinement Data for C₁₂H₁₂N₂O

CCDC Number	1906052
System, Space group, Z	Orthorhombic, P2 ₁ 2 ₁ 2 ₁ , 4
a, b, c (Å)	5.7203(10), 7.7326(14), 22.8219(42)
V(Å ³)	1009.48
D _x g.cm ⁻³	1.32
Radiation, λ, Å	0.71073
μ, mm ⁻¹	0.09
T, K	293
Sample size, mm ³	0.30 x 0.20 x 0.10
Diffractometer	Bruker APEX-II CCD
Scan mode	ω scan
T _{min} , T _{max}	0.915, 0.991
θ range, deg	1.78 to 25.99
h, k, l ranges	h = -7 to 7, k = -9 to 9, l = -28 to 27
Reflections total/unique	12684/1964
Reflections observed [I > 2σ(I)]	1835
R _{int}	0.028
F(000)	423.9
R	0.028
wR[F ²]	0.075
(Δσ) _{max}	0.024
Number of refined parameters	152
S	1.035
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.13, -0.13
Programs used	SHELXS97 ¹⁷ , SHELXL97 ¹⁷ , PARST ¹⁹ , PLATON ²⁰ , ORTEP ²¹ , MERCURY ²⁵

RESULTS AND DISCUSSION

The molecular structure containing atomic labeling is shown in Fig.-4 (ORTEP).²¹ The molecular structure consists of two benzene rings which are essentially planar, with atom C5 and C7 displaced out of their mean ring planes by -0.0071Å and -0.0025Å, respectively. Bond distances, bond angles and torsion angles which play an important role in collating the structural properties of the molecule are presented in Table-2.

Table-2: Bond Distances and Bond Angles.

Bond Distances(Å)		Bond Distances(Å)	
C1—C2	1.380 (2)	C9—C8	1.3783 (18)
C3—C2	1.386 (2)	C10—C9	1.3911 (18)
C4—C3	1.390 (2)	C10—N2	1.4022 (17)
C5—C4	1.380 (2)	C11—C10	1.3946 (18)
C6—C1	1.378 (2)	C11—C12	1.3831 (18)
C6—C5	1.3752 (18)	N1—C3	1.3875 (19)
C7—C8	1.3848 (19)	O1—C6	1.4002 (15)
C7—C12	1.3738 (18)	O1—C7	1.3881 (15)
Bond Angles(°)		Bond Angles(°)	
C6—C1—C2	119.88 (12)	C12—C7—C8	119.62 (11)
C1—C2—C3	120.97 (13)	C12—C7—O1	123.36 (12)

C2—C3—C4	118.01 (12)	C9—C8—C7	120.00 (11)
N1—C3—C2	121.28 (15)	C8—C9—C10	121.41 (12)
N1—C3—C4	120.70 (15)	C9—C10—C11	117.61 (12)
C5—C4—C3	121.37 (13)	C9—C10—N2	121.43 (12)
C6—C5—C4	119.44 (13)	C11—C10—N2	120.83 (12)
C1—C6—C5	120.31 (12)	C12—C11—C10	121.03 (11)
C1—C6—O1	118.97 (11)	C7—C12—C11	120.33 (12)
C5—C6—O1	120.63 (12)	C7—O1—C6	117.07 (9)
C8—C7—O1	116.96 (11)

Fig.-4: Ortep View of The Molecule with Displacement Ellipsoids Drawn at The 40% Probability Level. H Atoms Shown as Small Spheres of Arbitrary Radii.

All the bond distances are in normal range²² (except C3-N1 and C10-N2) and are comparable with the values observed for some analogous structures.^{23,24} The C3-N1 [1.387(19) Å] and C10-N2 [1.402(17) Å] bond distance is smaller than the standard value of 1.470 Å. The benzene ring A makes a dihedral angle of 79.44° with ring B.

In the crystal structure, there exist two intermolecular hydrogen bonds N2-H2A...O1 and N2-H2B...N2, respectively [Fig.-5] (Mercury).²⁵ Molecular packing in the unit cell as viewed down the a-axis is shown in Figure-6 (PLATON).²⁰ The details of intra/inter-molecular hydrogen bonds are given in Table-3. The N-H... π contacts as observed in the molecular packing are given in Table-4.

Table-3: Hydrogen Bonding Geometry (e.s.d.'s in parentheses)

D—H...A	D—H(Å)	H...A(Å)	D...A(Å)	D—H...A(°)
N2-H2A... O1 ⁱ	0.93	2.21	3.1299(6)	170
N2-H2B...N2 ⁱⁱ	0.91	2.37	3.2564(6)	165

Symmetry code: (i) x, 1 + y, z (ii) 1/2+x, 3/2-y, -z

Table-4: Geometry of N-H... π Interactions*

D—H...Cg	D—H(Å)	H...Cg(Å)	D...Cg (Å)	D—H...Cg (°)
N1-H1A...Cg1 ⁱ	0.85	2.92	3.7045(7)	153
N1-H1B...Cg2 ⁱⁱ	0.86	2.78	3.6421(7)	172

Symmetry code: (i) 1-x, -1/2 + y, 1/2 - z (ii) 2-x, -1/2 + y, 1/2 - z

Fig.-5: Intermolecular Hydrogen Bonds Link The Molecule.

Fig.-6: Packing of The Molecules Viewed Down The A-Axis.

* Cg1 represent the centre of gravity of benzene(A) ring.
Cg2 represents the center of gravity of benzene(B) ring.

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