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Crystal structure analysis and synthesis of 4-((2(2-bromophenoxy)Phenyl)ethynyl)-N,N-diethylaniline

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Abstract : Single crystals of4-((2(2-bromophenoxy)phenyl)ethynyl)-N,N-diethylaniline were grown by slow evaporation method and X-ray diffraction analysis reveals monoclinic P21/c space group with unit cell dimensions of a = 9.0761 (9) Å, b= 7.5220(7) Å, c= 30.468 (3) Å and β= 97.921(3)°.Crystal data were collected using BRUKER SMART APEX II CCDX-ray diffractometer. The structure was solved by direct method and refined on F^2 by full-matrixleast-squares procedure to the final R_1 of 0.051 using SHELXL programs.
Key Words : Bromophenoxy, Diethylaniline, Crystal packing and crystal structure.

Introduction

Diethylaniline is used as an intermediate in the manufacture of dyes, pharmaceuticals and other chemicals, and also as a reaction catalyst. In organic synthesis, the complex diethylaniline borane (DEANB) is used as a reducing agent[1].Diethylaniline may be genotoxic because it has been found to increase the rate of sister chromatid exchange[2].In genetics, genotoxicity describes the property of chemical agents that damages the genetic information within a cell causing mutations, which may lead to cancer. While genotoxicity is often confused with mutagenicity, all mutagens are genotoxic, whereas not all genotoxic substances are mutagenic. The alteration can have direct or indirect effects on the DNA the induction of mutations, mistimed event activation, and direct DNA damage leading to mutations. The permanent, heritable changes can affect either somatic cells of the organism or germ cells to be passed on to future generations[3].

Experimental

X-ray Structure Determination

Single crystal of the compound suitable for x-ray diffraction was obtained by slow evaporation method. Three dimensional intensity data were collected on a Bruker[5] SMART APEX CCD Diffractometer using graphite monochromatized Mo-Kα radiation (λ= 0.71073 Å) at Department of chemistry, IIT, Chennai, India. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXL programs[6]. All the non-hydrogen atoms were refined usingisotropic and later anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with ORTEP-3[7].The crystallographic data for the compound are listed in Table 1.

Synthesis of the compound

To a dry two neck 50 ml RB flask, $PdCl_2$ $(PPh_3)_2$ (3 mol-%) and CuI (3 mol-%) were added to the dissolved aryl iodide **1** (0.50 mmol,) in NEt_3 under nitrogen atmosphere and stirred another 10 minutes in room temperature. Then, dissolved solution of alkyne**2**in NEt_3 (0.50 mmol,) was added to reaction mixture and stirred another 6h (monitored by TLC). After completion, the reaction mixture was filtered through celite pad and washed with EtOAc, evaporated solvent under reduced pressure. The residue purified by siliga gel column chromatography on eluting with petroleum ether/ethyl acetate (0 - 10%) to afford product **3** in 80 % yield.

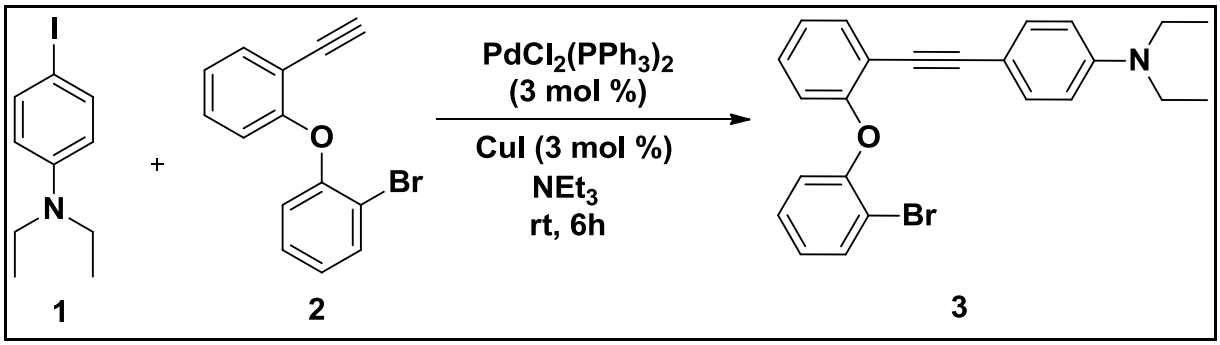

Table 1: Crystal data and structure refinement of the titled compound

Compound	**Parameters**
Empirical formula	$C_{24}H_{22}$ Br N O
Formula weight	420.33
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 9.0761(9) Åalpha = 90º b = 7.5220(7) Å beta = 97.921º c = 30.468(3) Ågamma = 90º
Volume	2060.2(3) $Å^3$
Z, Calculated density	4, 1.355 Mg/m^3
Absorption coefficient	2.008 mm^{-1}
F(000)	864
Crystal size	0.30 x 0.25 x 0.20 mm
Theta range for data collection	2.27 to 21.87 deg.
Limiting indices	-6<=h<=9, -7<=k<=7, -25<=l<=31.
Reflections collected / unique	4691 / 2442 [R(int) = 0.0264]
Completeness to theta = 21.87	98.2%
Max. and min. transmission	0.669 and 0.553
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2442 / 0 / 246
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	**R1 = 0.0518**, wR2 = 0.1175
R indices (all data)	R1 = 0.0715, wR2 = 0.1257
Extinction coefficient	0.0023(4)
Largest diff. peak and hole	0.418 and -0.587 e. $Å^{-3}$

Results and Discussion

In the title compound $C_{48}H_{44}Br_2N_2O_2$the dihedral angle between the mean planes of the bromophenoxy ring and the phenyl ring system is 84.9(3)°.They are slightly twisted out of the plane of the N-methylethanamine moiety with torsion angles ofC-C-N-C and C-N-C-C-93.3(5) and -85.4(5), indicating a (-) anti-clinal and (-) syn-clinal conformation for this groups. Two phenyl rings (C7-C12, C15-C20) are coplanar with making dihedral angle of 2.5(2)°. The bromine and oxygen atoms deviate from phenyl ring by -0.036 and -0.141Å, respectively.The crystal structure stabilized by C4-H4…Cg2,C11-H11…Cg3 and C17-H17…Cg3 intermolecular interactions of Cg2 and Cg3.The symmetry codes i) x,-1+y,z;ii) 1-x,1/2+y,1/2-z; iii) -x,-1/2+y,1/2-z. The packing view of the title compound is shown in fig. (2)

Table 2: Hydrogen-bond geometry [Å]

D—H…A	D—H	H…A	D…A	D—H…A
C4-H4…Cg2^{i}	0.93	2.89	3.752(7)	154
C11-H11…Cg3^{ii}	0.93	2.85	3.646(5)	144
C17-H17…Cg3^{iii}	0.93	2.88	3.664(5)	143
C19-H19…Cg2^{ii}	0.93	2.90	3.696(5)	144

Symmetry code:

i) x,-1+y,z

ii) 1-x,1/2+y,1/2-z

iii) -x,-1/2+y,1/2-z

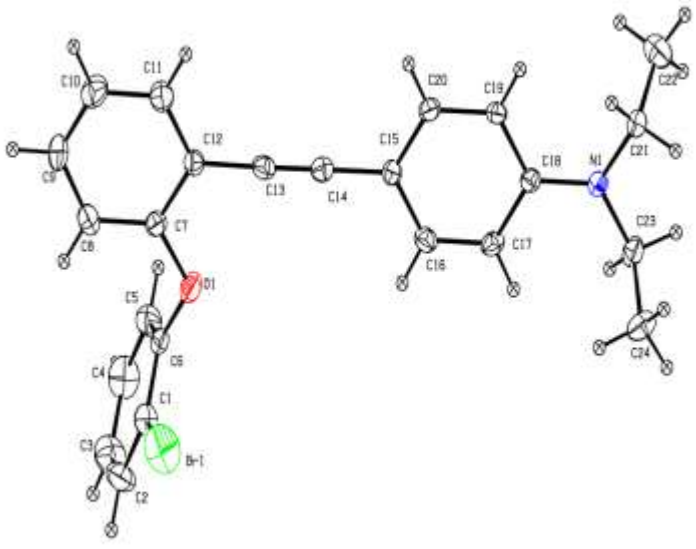

Fig.1. The molecular structure of the title compound with atom labeling. Displacement ellipsoids are drawn at the 30% probability level.

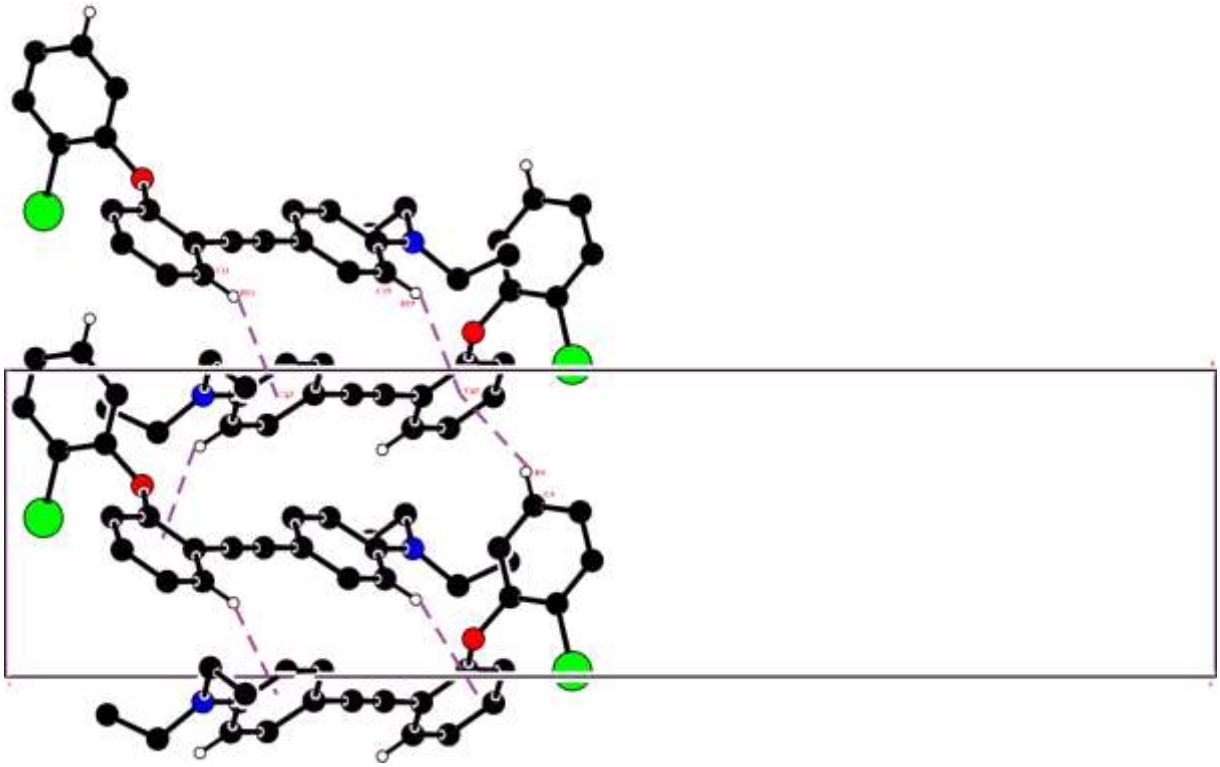

Fig.2. The crystal packing of the titled compound forming C-H…π interactions viewed along aaxis. The hydrogen bonds are shown as dashed lines(see Table 2 for details).

Table 3: Selected Bond lengths (Å)

Atom	Length	Atom	Length
C(1)-C(2)	1.384(7)	C(13)-C(14)	1.194(6)
C(1)-Br(1)	1.880(5)	C(14)-C(15)	1.425(7)
C(1)-C(6)	1.376(6)	C(18)-N(1)	1.375(5)
C(6)-O(1)	1.381(6)	C(21)-N(1)	1.450(6)
C(7)-O(1)	1.376(5)	C(23)-N(1)	1.458(6)
C(5)-C(6)	1.355(7)	C(21)-C(22)	1.515(7)
C(12)-C(13)	1.430(7)	C(23)-C(24)	1.518(7)

Table 4: Selected Bond angles (º)

Atom	Angle	Atom	Angle
C(6)-C(1)-C(2)	119.4(5)	N(1)-C(21)-H(21A)	108.9
C(6)-C(1)-Br(1)	120.5(4)	H(21A)-C(21)-H(21B)	107.7
C(2)-C(1)-Br(1)	120.0(4)	N(1)-C(23)-C(24)	113.3(4)
C(1)-C(2)-H(2)	120.2	N(1)-C(23)-H(23B)	108.9
C(1)-C(6)-O(1)	118.2(5)	H(24B)-C(24)-H(24C)	109.5
C(11)-C(10)-H(10)	120.0	C(18)-N(1)-C(23)	121.6(4)
N(1)-C(18)-C(19)	121.9(4)	C(21)-N(1)-C(23)	116.7(4)
N(1)-C(21)-C(22)	113.3(4)	C(7)-O(1)-C(6)	119.3(3)

Conclusion

The crystal structure analysis of a novel ethynyl and aniline compound was studied using x-ray diffraction method. In the compound, the crystal packing is stabilized by intermolecular C—H…π hydrogen bonds.

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