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Crystal structure analysis of 1,1'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(methylene))bis(4-((3,5-bis(chloromethyl) phenoxy)methyl)-1H-1,2,3-triazole)

K. Elumalai[1], Devaraj Anandkumar[2], Perumal Rajakumar[2], K. Sakthi Murugesan[1]*

[1]Department of Physics, Presidency College (Autonomous), Chennai-600 005, India
[2]Department of Organic Chemistry, University of Madras, Chennai 600 025, India

Abstract: The crystal structure of 1,1'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(methylene))bis(4-((3,5-bis(chloromethyl)phenoxy)methyl)-1H-1,2,3-triazole) ($C_{49}H_{56}Cl_4N_6O_2$). The compound crystallizes in Triclinic P-1 space group with unit cell parameters at 296(2) K as follows: a = 13.1712(3)Å, b = 13.8053(3) Å, c= 13.9774(3)Å, α = 84.140(1)°, β= 71.691(1)° γ = 86.727(1)°. Crystal data were collected using BRUKER SMART APEX II CCD X-ray diffractometer. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures to the final R_1 of 0.065 using SHELXL programs.
Key Words: triazole, methylene and crystal structure.

Introduction

Triazoles and triazole derivatives play an important role in pharmaceuticals, agrochemicals, dyes, photographic materials, and in corrosion inhibition and have many biological applications[1,2,3]. Naphthalene derivatives has been identified as new range of potent antimicrobials effective against wide range of human pathogens and have diverse and interesting antibiotic properties with minimum toxicity[4,5].

Experimental

X-ray Structure Determination

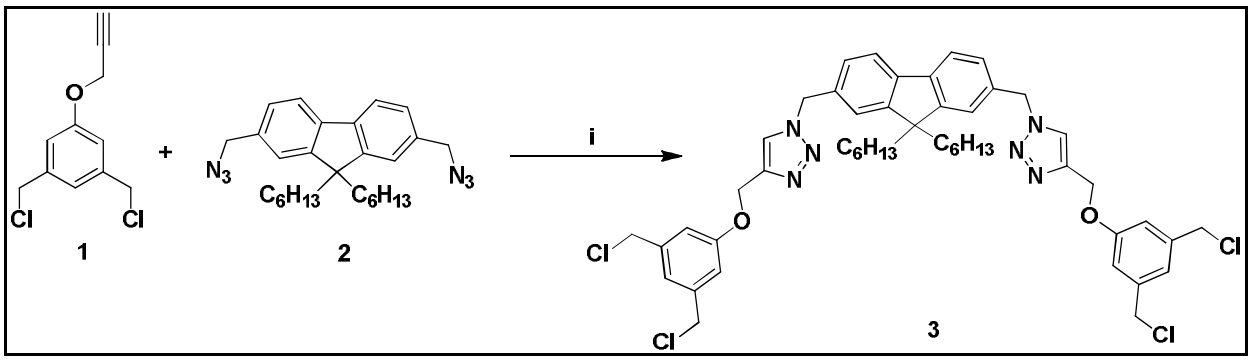
Single crystal of the compound suitable for x-ray diffraction was obtained by slow evaporation method. Three dimensional intensity data were collected on a Bruker[6] SMART APEX CCD Diffractometer using graphite monochromatized Mo-Kα radiation (λ= 0.71073 Å) at Department of chemistry, IIT, Chennai, India. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXL programs[7]. All the non-hydrogen atoms were refined using isotropic 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[8]. The crystallographic data for the compound are listed in Table 1.

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

Compound	**Parameters**
Empirical formula	$C_{49}\ H_{56}\ Cl_4\ N_6\ O_2$
Formula weight	902.80
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 13.1712(3) Å alpha = 84.1400(10) deg. b = 13.8053(3) Å beta = 71.6910(10) deg. c = 13.9774(3) Å gamma = 86.7270(10) deg.
Volume	2399.43(9) $Å^3$
Z, Calculated density	8, 1.250 Mg/m^3
Absorption coefficient	0.291 mm^{-1}
F(000)	952
Crystal size	25 x 30 x 20 mm
Theta range for data collection	1.48 to 25.00 deg.
Limiting indices	-15<=h<=15, -16<=k<=16, -14<=l<=16
Reflections collected / unique	34564 / 8451 [R(int) = 0.0223]
Completeness to theta = 25.00	100.00%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8451 / 0 / 558
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	**R1 = 0.0657**, wR2 = 0.1767
R indices (all data)	R1 = 0.0962, wR2 = 0.2025
Largest diff. peak and hole	0.716 and -0.614 e. $Å^{-3}$

Synthesis of the compound

The reaction of 2,7-bis(azidomethyl)-9,9-dihexyl-9*H*-fluorene **2** (1.0 equiv) with 2.1 equivalents of 1,3-bis(chloromethyl)-5-(propargyloxy)- benzene **1** under Cu(I) catalyzed click reaction conditions $CuSO_4 \cdot 5H_2O$ and sodium L-ascorbate were stirred at room temperature for 18 h in THF/water. After confirming the completion of reaction on TLC, ethyl acetate was added to the reaction mixture and washed with water (10 mL), and brine (10 mL). The separated organic layer was dried over Na_2SO_4 and evaporated to obtain the crude product. Purification was done by flash chromatography. Finally gave the pure compound of first generation chloro dendrimer **3.**



Results and Discussion

The symmetric unit of the title compound is shown in Fig. 1. The two fused phenyl and cyclopentane rings are approximately planar, making dihedral angle of 1.47(17)° and 1.56(17)°, respectively. The molecule is twisted with the benzene ring and the mean plane through the fused two triazole ring system be inclined to one another by 87.06(18)° and 89.5(2)°, respectively. The methylene groups assume a twisted conformation, as can be seen from the torsion angle C26-C27-C28-C29 = 173.5(6)° and C20-C21-C22-C23 = -176.5(4)°, indicating a (+) Anti-periplanar and (-) Anti-periplanar conformation for this group. Atoms O1 and O2 deviated from the respective two phenyl rings by -0.012 Å and -0.061 Å, respectively.

In the crystal, molecules are linked by C---H…N hydrogen bond to form chains propagating along the b axis direction. The crystal packing is further stabilizing by C---H... Cl intermolecular interactions. The chains are linked by slipped parallel $\pi \cdots \pi$ interactions, invoving inversion related chloromethyl phenoxy methyl rings, forming slabs parallel to the bc plane Cg4-Cg4^{1} = 3.903 Å, inter-planar distance = -3.5087(15) Å, slippage = 1.708 Å Cg4 is the centroid of ring (C2-C3-C4-C6-C7-C8). The selected bond lengths and angles are listed in table 3 and 4, respectively.

Table 2: Hydrogen-bond geometry [Å]

Distance (Å)				Angle (°)
D—H…A	D—H	H…A	D…A	D—H…A
C9---H9A…N6	0.97	2.51	3.382(4)	149
C39---H39…Cl2	0.93	2.79	3.715(3)	170

Symmetry code: i. x, y, 1+z, ii. x,1+y,-1+z

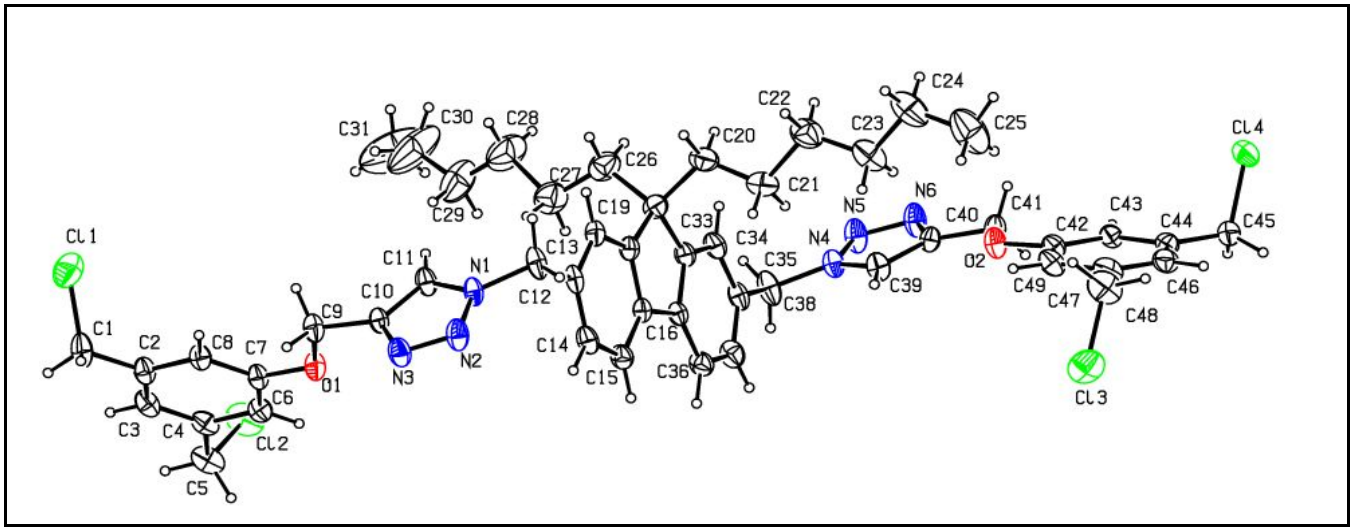


Fig.1. The molecular structure of the title compound, with the atom-numbering scheme. The displacement ellipsoids are drawn at 30% probability level. H atoms are shown as spheres of arbitrary radius.

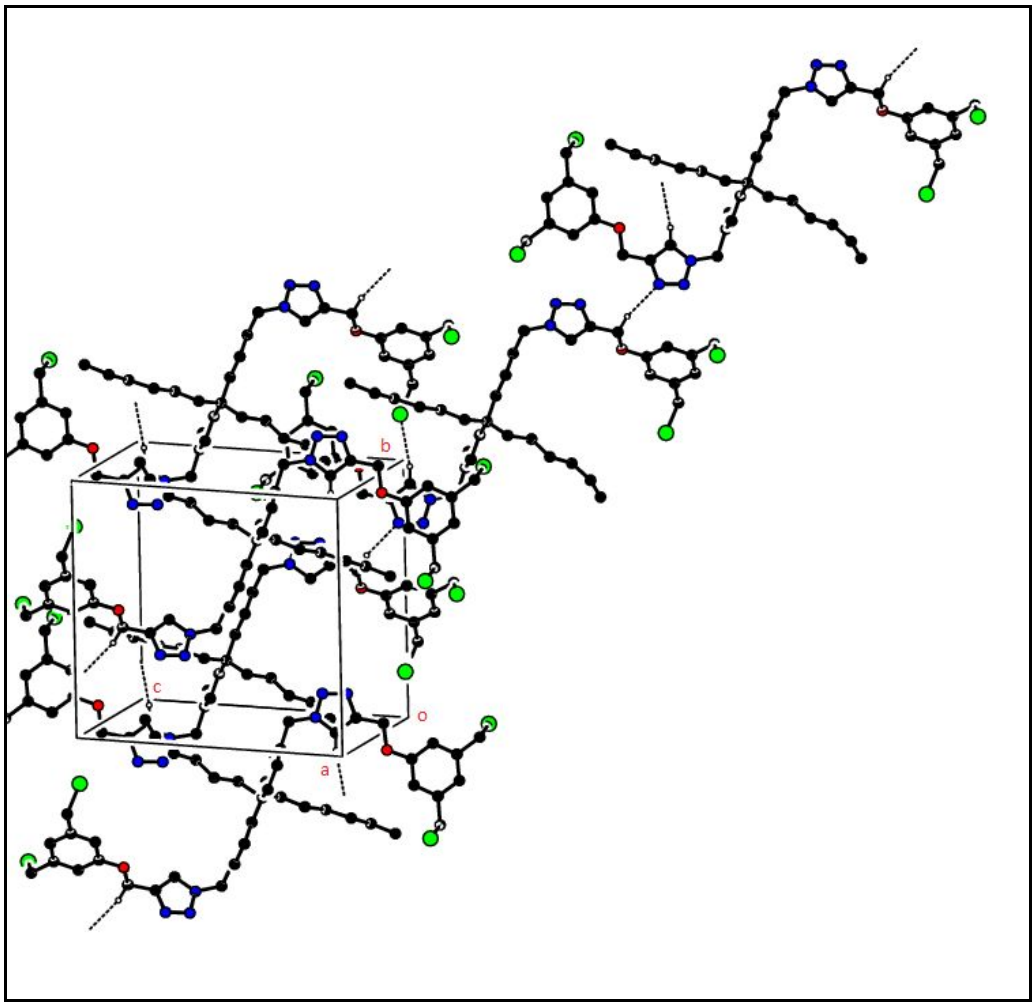


Fig.2. The crystal packing of the title compound, viewed along b axis, showing C---H...N hydrogen bonds. The hydrogen bonds are shown as dashed lines (see Table 2 for details).

Table 3: Selected Bond lengths (Å) **Table 4: Selected Bond angles (º)**

Bond	Length (Å)	Bond	Angle (°)
C(1)-C(2)	1.508(5)	C(2)-C(1)-Cl(1)	113.0(3)
C(1)-Cl(1)	1.773(5)	C(2)-C(1)-H(1A)	109
C(1)-H(1A)	0.97	Cl(1)-C(1)-H(1A)	109
C(1)-H(1B)	0.97	C(2)-C(1)-H(1B)	109
C(2)-C(3)	1.380(5)	Cl(1)-C(1)-H(1B)	109
C(2)-C(8)	1.387(4)	H(1A)-C(1)-H(1B)	107.8
C(3)-C(4)	1.379(5)	C(3)-C(2)-C(8)	119.7(3)
C(3)-H(3)	0.93	C(3)-C(2)-C(1)	121.0(3)
C(4)-C(6)	1.378(5)	C(8)-C(2)-C(1)	119.3(3)
C(4)-C(5)	1.512(5)	C(4)-C(3)-C(2)	120.6(3)
C(5)-Cl(2)	1.764(4)	C(4)-C(3)-H(3)	119.7
C(5)-H(5A)	0.97	C(2)-C(3)-H(3)	119.7
C(5)-H(5B)	0.97	C(6)-C(4)-C(3)	119.7(3)
C(6)-C(7)	1.383(5)	C(6)-C(4)-C(5)	119.7(4)
C(6)-H(6)	0.93	C(3)-C(4)-C(5)	120.6(3)
C(7)-O(1)	1.373(4)	C(4)-C(5)-Cl(2)	112.7(3)

C(7)-C(8)	1.381(5)	C(4)-C(5)-H(5A)	109.1
C(8)-H(8)	0.93	Cl(2)-C(5)-H(5A)	109.1
C(9)-O(1)	1.423(4)	C(4)-C(5)-H(5B)	109.1
C(9)-C(10)	1.483(4)	Cl(2)-C(5)-H(5B)	109.1
C(9)-H(9A)	0.97	H(5A)-C(5)-H(5B)	107.8
C(9)-H(9B)	0.97	C(4)-C(6)-C(7)	120.1(3)
C(10)-N(3)	1.343(4)	C(4)-C(6)-H(6)	119.9
C(10)-C(11)	1.357(4)	C(7)-C(6)-H(6)	119.9
C(11)-N(1)	1.335(4)	O(1)-C(7)-C(8)	123.7(3)
C(11)-H(11)	0.93	O(1)-C(7)-C(6)	116.1(3)
C(12)-N(1)	1.470(4)	C(8)-C(7)-C(6)	120.2(3)
C(12)-C(13)	1.514(4)	C(7)-C(8)-C(2)	119.7(3)
C(12)-H(12A)	0.97	C(7)-C(8)-H(8)	120.1
C(12)-H(12B)	0.97	C(2)-C(8)-H(8)	120.1
C(13)-C(14)	1.375(5)	O(1)-C(9)-C(10)	109.5(3)
C(13)-C(18)	1.384(5)	O(1)-C(9)-H(9A)	109.8

Conclusion

The crystal structure analysis of a novel triazole compound was studied using x-ray diffraction method. In the crystal, molecules are linked via C---H...N hydrogen bonds, forms chains. The crystal packing is further stabilized by C---H... $\boldsymbol{\pi}$ and $\boldsymbol{\pi}$---$\boldsymbol{\pi}$ intermolecular interactions.

Acknowledgments

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