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Synthesis, Molecular Structure from the X-ray Diffraction Data of the Powder (1*E*,1'*E*)-1,1'-(1,4-Phenylene)Bis(*N*-(Adamantan-1-yl)methanimine)

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Abstract

The title compound was synthesized by condensation between two equivalents adamantan-1-ylamine and one equivalent of benzene-1,4-dicarbaldehyde in *n*-BuOH and produced a good yield 87% of new bis Schiff base. The compound skeleton was affirmed by FTIR, ¹H NMR, LC-MS, and X-ray powder diffraction. The structure was solved by a parallel tempering process and refined by using Rietveld refinement. Two adamantan-1-ylimino groups are connected in the anti-positions to the planar central 1,4-dimethylbenzene group. All rings of the adamantyl group possess normal chair conformation.

Keywords: Powder X-ray diffraction, Adamantan-1-ylamine, Bis Schiff base.

تحضير , التركيب الجزيئي من بيانات حيود الأشعة السينية لمسحوق (1*E*,1'*E*)-1,1'-(4,1)-فينيلين) بس (N-آدامنتان-1-يل) ميثانامين

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الخلاصة

حضر المركب المعنون من تكاثف بين مكافئين من أمين آدامنتان-1-يل ومكافئ واحد من البنزين-4,1-ثنائي كاربالديهايد في البيوتان الاعتيادي ونتج بنسبة جيدة 87% لقاعدة شف الثنائية الجديدة. شخخص التركيب باستخدام مطيافية الأشعة تحت الحمراء, الرنين النووي المغناطيسي البروتوني, طيف الكتلة كروماتوغرافيا السائل, وتحليل حيود الأشعة السينية للمسحوق. تم حل التركيب بطريقة التقسية المتوازية وتم صقله باستخدام صقل ريتفيلد. ترتبط مجموعتي آدامنتان-1-يل ايمينو بوضعيات متقابلة بالنسبة للمستوى المركزي لمجموعة 4,1-ثنائي مثل بنزين. تمتلك جميع حلقات مجموعة الأدامنتيل وضعية الكرسي الاعتيادية.

Introduction

The molecular design of adamantane and its derivatives are actual importance for researchers in molecular technology. Adamantan-1-ylamine is an alicyclic tricyclic amine which has an unusual skeleton adamantyl fragment consisting of three fused cyclohexane rings in a chair conformation [1]. It is the smallest repeating fragment of the diamond lattice [2]. The synthesis of molecules containing two or more pharmaceutical fragments in their structure allows for the development of new types of biological properties and for the extension of known curative effects. Adamantan-1-amine and its derivatives have been a good source for a wide scope of pharmaceutical drugs. In particular, they have

been effective in the development of drugs for Parkinson's disease [3], treatment and protection against influenza virus (A) [4], anti-microbial drugs [5], and anti-inflammatory drugs [6]. Furthermore, compounds that contain azomethines are reactive intermediates for organic synthesis in different fields and have biological [7, 8], anti-viral [9], anti-bacterial [10,11], and anti-fungal [12] effects, as well as inhibiting anti-microbial agents [13]. A search in the CCDC Database survey gave few results containing adamantan-1-ylaminomethylbenzene fragment or 1,4-di(aminomethyl)benzene fragment [14-20]. Structures similar to the title compound are absent in the database. This work presents new applications of bis imine (*1E,1'E*)-1,1'-(1,4-phenylene)*bis*(*N*-(adamantan-1-yl)methanimine) as a predecessor for the synthesis of new compounds. The structure of the desired compound was confirmed by the use of the X-ray powder diffraction technique.

Materials and Methods

The materials were purchased from Merck (Germany) and Romil Co. (UK). The melting point was measured by the Stuart SMP-10 apparatus. FTIR, ^1H NMR and LC-MS spectra were recorded on Bruker Tensor 27, Bruker UltraShield (300 MHz, CDCl_3), and Thermo Scientific Exactive Plus Orbitrap LC-MS spectrometer, respectively. X-ray powder diffraction pattern was measured on the PANalytical Empyrean diffractometer.

Synthesis of the title compound

To a hot solution of adamantan-1-ylamine (4 g, 0.026 mol) in 15 ml *n*-BuOH a solution of benzene-1,4-dicarbaldehyde (1.74 g, 0.013 mol) in 10 ml *n*-BuOH was added. The mixture was refluxed with stirring for 30 min and was then left for 3 h. The crude product was filtered and evaporated. The product was collected and re-crystallized from EtOH or *i*-PrOH.

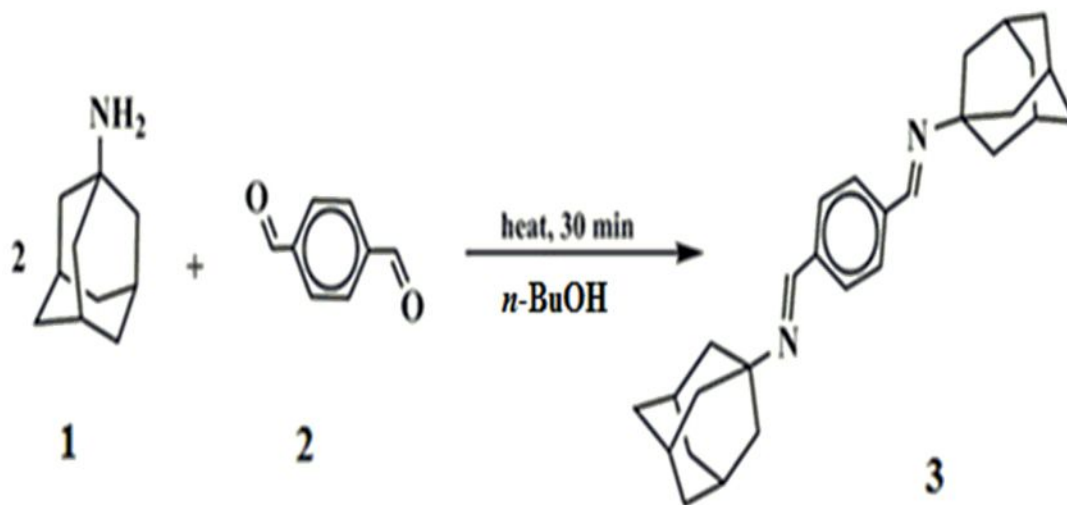
The properties and spectral data of the title compound:

White needles, yield 4.6 g (87%), m.p 243–244°C. FTIR, ν , cm^{-1} : 1633 (C=N), 3013 (C—H aromatic), 2904, 2846 (C—H aliphatic). ^1H NMR (CDCl_3 , δ , 300 MHz, p.p.m.): (adamantyl group 1.66 (s, 12H, 6 CH_2), 1.85 (m, 6H, 6CH), 2.23 (broad s, 12H, 6 CH_2)), 7.92–8.26 (m, 4H, Ar-ring), 8.32 (s, 2H, 2 CH=N). LC-MS, m/z (%): 400.89 [M] $^+$ (100).

X-ray powder structure of the title compound: The powder as very small needles was obtained by allowing the saturated EtOH solution of the compound to stand for four days. The details of crystallographic data are shown in Tables 1-4.

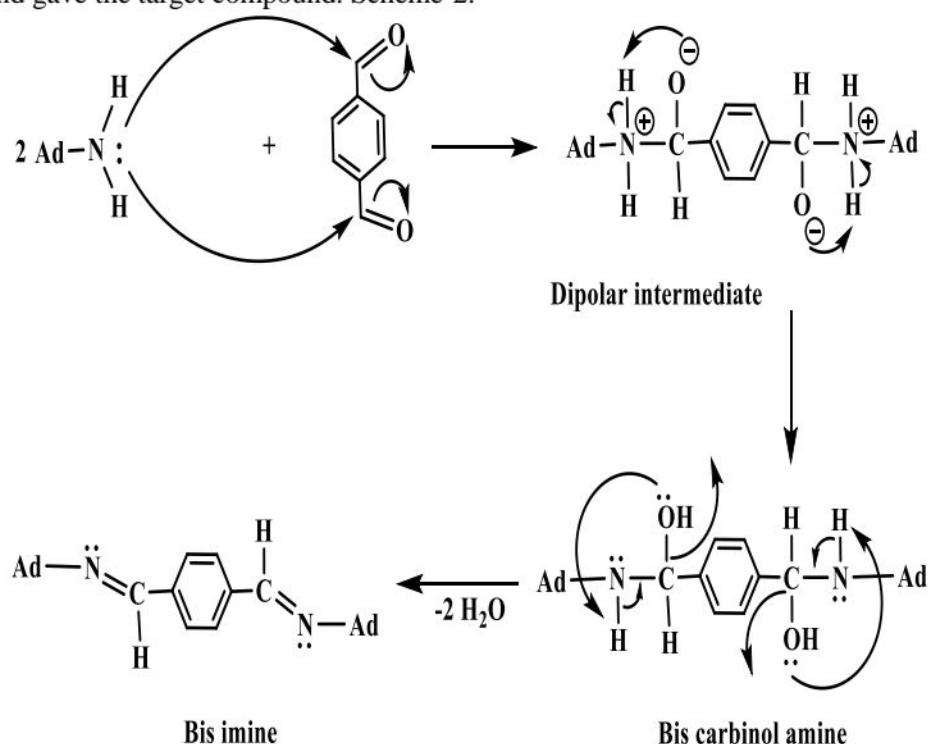
Results and Discussion

The route of the synthesis of the title compound is shown in scheme 1, which includes the synthesis of new bis Schiff base (*1E,1'E*)-1,1'-(1,4-phenylene)*bis*(*N*-(adamantan-1-yl)methanimine) by condensation between two equivalents adamantan-1-ylamine and one equivalent of benzene-1,4-dicarbaldehyde in the presence of *n*-butanol as a solvent, and produced a good yield (87%). The skeleton of the compound was affirmed by FTIR, ^1H NMR, LC-MS, and powder X-ray diffraction.



Scheme 1- For the synthesis of the title structure

FTIR spectrum displayed evanescence in the stretching vibration bands of groups (-NH₂) and (C=O) for amine and benzene-1,4-dicarbaldehyde respectively with appeared stretching vibration band of the azomethine group (C=N) at 1633 cm⁻¹. The stretching vibration band for (C-H_{aromatic}) appeared at 3013 cm⁻¹, and stretching vibration bands for (C-H_{aliphatic}) appeared at 2846 and 2904 cm⁻¹ (Figure-1). The ¹H NMR spectrum for (2CH=N) protons displayed the presence of a down-field singlet at δ 8.32 ppm and protons of phenyl group displayed two singlets at δ 7.92 and 8.26 ppm. The adamantyl group exhibited signals as a singlet, multiplet, and broad singlet at δ 1.66 (12H, 6CH₂C-N), 1.85 (6H, 6CH) and 2.23 (12H, 6CH₂) ppm, respectively (Figure-2). Moreover, LC—mass spectrum was identical to its molecular weight, m/z (%): 400.89 [M]⁺ (100) (Figure-3). The formation of the bis imine derivative title compound was occurred according to a similar suggested mechanism in literature [12] but in the absent catalyst. The two pairs of electrons nitrogen of two molecules amine attacks to the dicarbonyl group by nucleophilic addition produced dihemiaminal and then the left two water molecules and gave the target compound. Scheme-2.



Ad=adamantyl group

Scheme 2-The suggested mechanism of bis imine for target compound

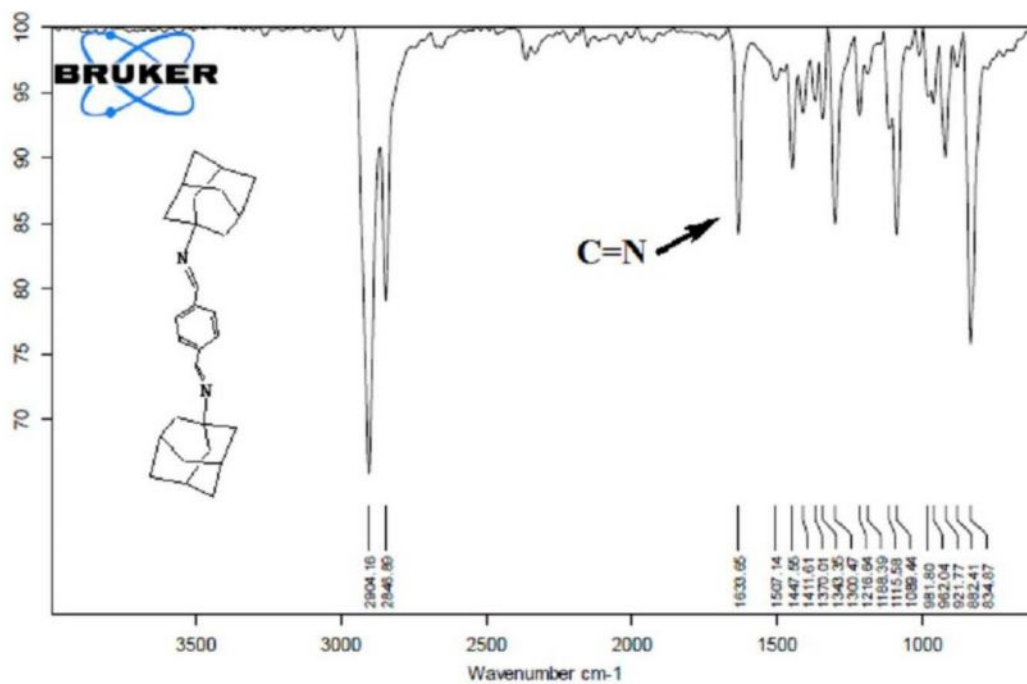


Figure 1-FTIR spectrum of the title compound

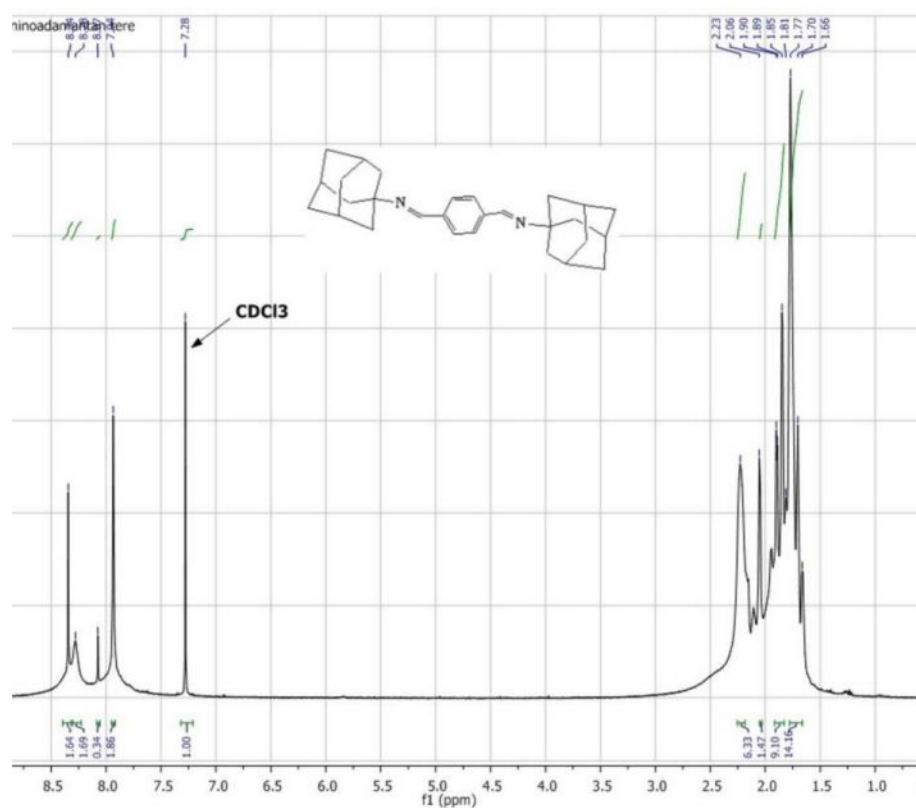


Figure 2-¹H NMR spectrum of the title compound

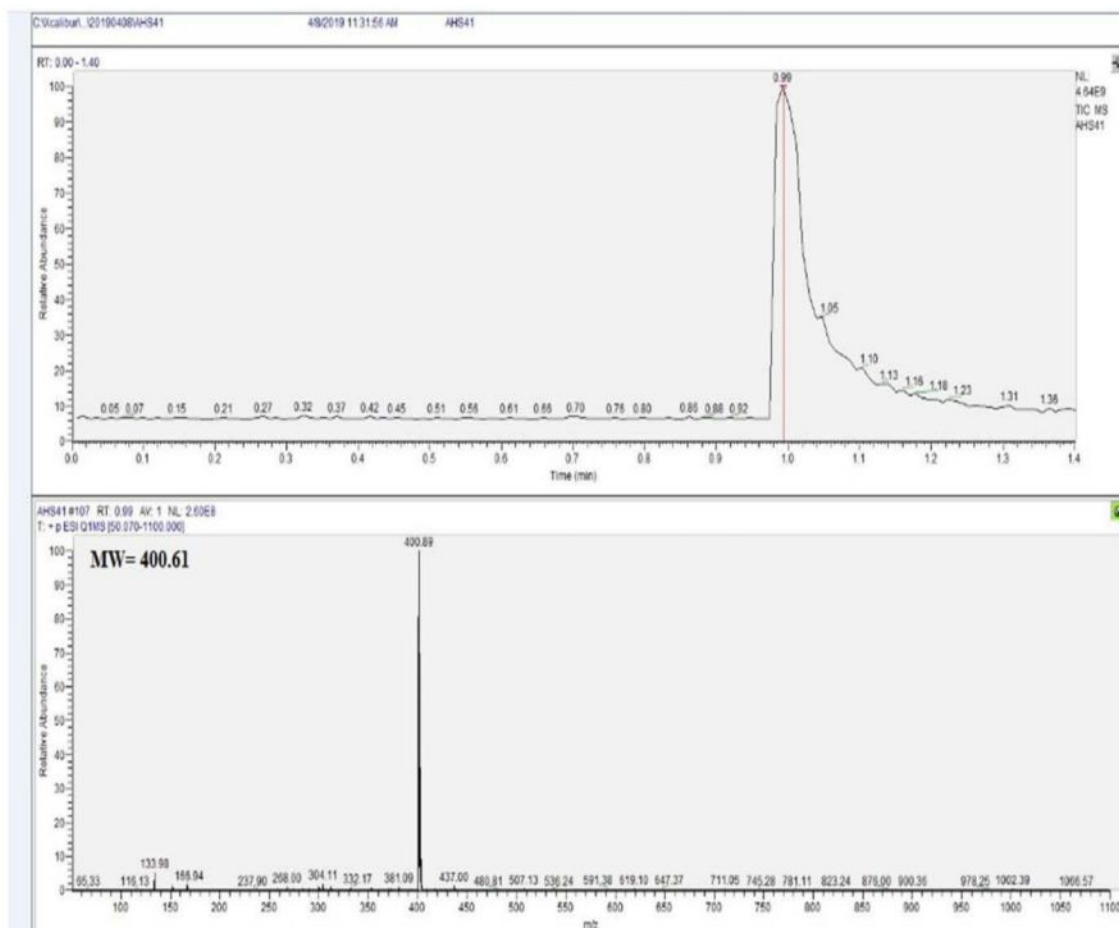


Figure 3-LC-MS spectrum of the title compound

Crystallographic Study

The molecular structure of the title compound was displayed in Figure- 4. Its crystalline data were as follows: $C_{28}H_{36}N_2$, $M.W= 400.59 \text{ g.mol}^{-1}$, system with space group: Monoclinic, $C2/c$, $a=28.249$ (10) \AA , $b= 6.450$ (18) \AA , $c= 12.509$ (4) \AA , $\beta= 91.88$ (4), $V=2278$ (6) \AA^3 , $Z= 4$, Rad. type $Cu K\alpha$, $\lambda = 1.5418 \text{\AA}$, Specimen shape, size: Flat sheet (15 \times 1) mm.

The X-ray powder diffraction pattern in (Figure-6) was measured by computer programs in the θ range 5-70 $^\circ$ on PANalytical Empyrean diffractometer [21]. The structure was solved by parallel tempering technique using FOX [22], and refined by Rietveld refinement procedure was made by MRIA [23] with constrained isotropic thermal parameters for all non-hydrogen atoms. Molecular graphics was made by Mercury [24]. Hydrogen atoms were calculated and not refined. The bond length of (N6-C12) for (N=C) is normal 1.32 (2) \AA . In the crystal structure of the target compound, was observed two adamantan-1-ylimino groups are arranged in the anti-positions to the planar central 1, 4-dimethylbenzene group (Figure-4). The molecule is located on the inversion center. All rings of adamantyl moiety possess normal chair conformation. The details of the crystal data are provided in Tables-(1-4).

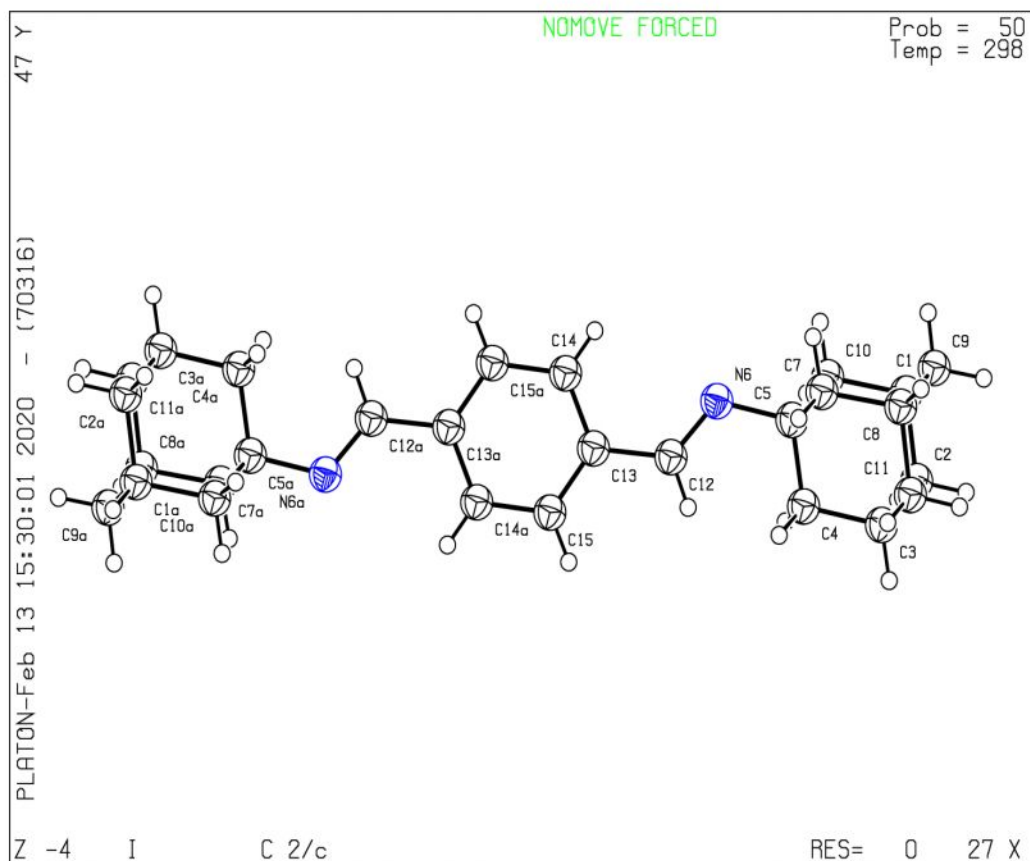


Figure 4-Data block: Showing the molecular structure, atoms numbering and displacement ellipsoids are drawn at 50% probability level of the title compound

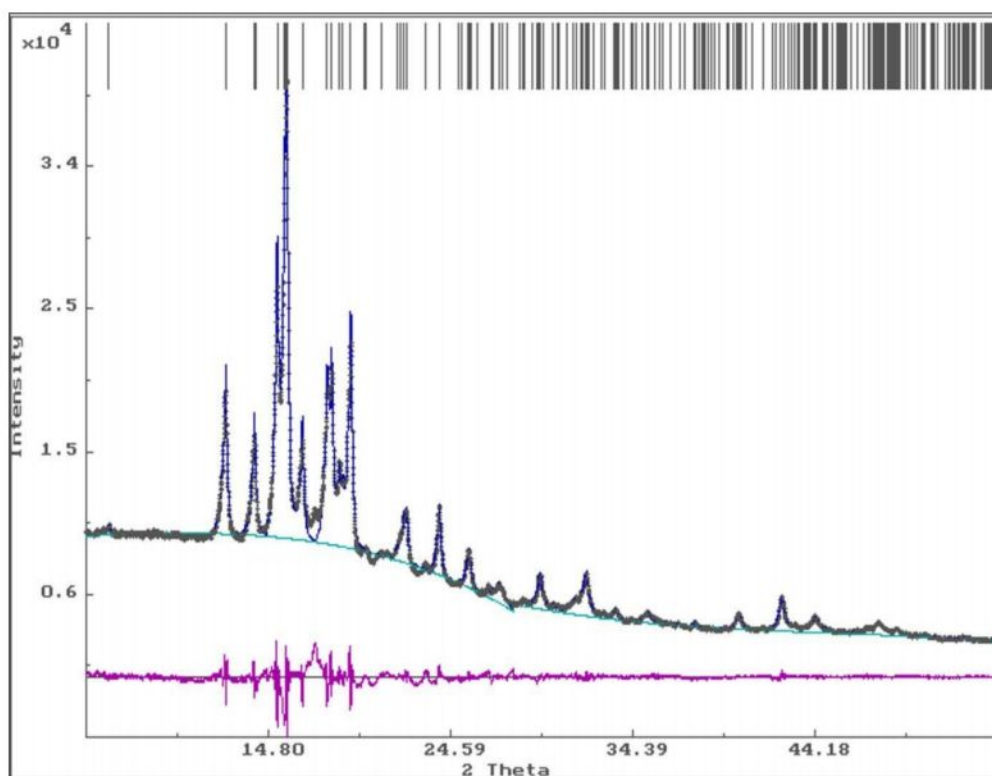


Figure 5-Powder diffraction pattern of the title compound

Table 1-Crystal data and refinement details of the title compound

Crystal data	
<i>M.F</i>	C ₂₈ H ₃₆ N ₂
<i>M.W</i>	400.59
Crystal system and group of space	Monoclinic, C2/c
Temp.	298 K
<i>a, b, c</i> (Å)	28.249 (10), 6.450 (18), 12.509 (4)
β (°)	91.88 (4)
<i>V</i> (Å ³)	2278 (6)
<i>Z</i>	4
Type of radiation	Cu <i>K</i> α , λ =1.5418 Å
Shape and size of specimen	Flat sheet, 15×1 mm
Collection data	
Diffractometer	EMPYREAN (PANalytical, 2011)
Mounting of specimen	Thin layer over the non-diffracting silicon plate
Mode collection data	Reflection
Scan process	Persistent
2 θ values	2 θ_{\min} = 5.00°, 2 θ_{\max} = 70.00°, 2 θ_{step} = 0.01°
Refinement	
R-factors and quality of fit	R _p =0.026, R _{wp} =0.033, R _{exp} =0.013, R _{Bragg} =0.109°, χ^2 =7.618
Parameters number	104
Restraints number	48
Treatment of H-atoms	Parameters of H-atoms not refined
Code of symmetry	(i) ^{-x, -y+1, -z+1}
CCDC reference, deposition number	1971146

Table 2-Geometric parameters (Bonds lengths) (Å, °) of the title compound

Bond	<i>d</i> (Å, °)	Bond	<i>d</i> (Å, °)
C1-C2	1.534 (19)	C1-H1	0.9800
C1-C9	1.57 (3)	C2-H2A	0.9700
C1-C10	1.54 (3)	C2-H2B	0.9700
C2-C3	1.55 (2)	C3-H3	0.9800
C3-C4	1.535 (19)	C4-H4A	0.9700
C3-C11	1.54 (2)	C4-H4B	0.9700
C4-C5	1.528 (16)	C7-H7A	0.9700
C5-N6	1.48 (2)	C7-H7B	0.9700
C5-C7	1.54 (2)	C8-H8	0.9800
C5-C10	1.55 (2)	C9-H9A	0.9700
N6-C12	1.32 (2)	C9-H9B	0.9700
C7-C8	1.541 (19)	C10-H10A	0.9700
C8-C9	1.555 (19)	C10-H10B	0.9700
C8-C11	1.555 (17)	C11-H11A	0.9700
C12-C13	1.501 (18)	C11-H11B	0.9700
C13-C14	1.41 (3)	C12-H12	0.9300
C13-C15	1.39 (2)	C14-H14	0.9300
C14-C15i	1.4213 (2)	C15-H15	0.9300
C15-C14i	1.4213 (2)		

Table 3- Geometric parameters (Bonds angles ω , °) of the title compound

Angle	ω , °	Angle	ω , °
C2-C1-C9	106.5 (7)	C11-C3-H3	110.5
C2-C1-C10	108.1 (5)	C2-C3-H3	110.5
C9-C1-C10	104.9 (4)	C5-C4-H4A	109.7
C1-C2-C3	112.5 (3)	C3-C4-H4A	109.7
C2-C3-C4	107.1 (3)	C5-C4-H4B	109.7
C2-C3-C11	109.7 (5)	C3-C4-H4B	109.7
C4-C3-C11	108.6 (3)	H4A-C4-H4B	108.2
C3-C4-C5	110.0 (5)	C5-C7-H7A	109.3
C4-C5-N6	111.0 (9)	C8-C7-H7A	109.3
C4-C5-C7	111.9 (6)	C5-C7-H7B	109.3
C4-C5-C10	107.4 (4)	C8-C7-H7B	109.3
N6-C5-C7	108.4 (8)	H7A-C7-H7B	108.0
N6-C5-C10	108.0 (6)	C7-C8-H8	112.9
C7-C5-C10	109.9 (2)	C9-C8-H8	112.9
C5-N6-C12	119.4 (2)	C11-C8-H8	112.9
C5-C7-C8	111.6 (8)	C8-C9-H9A	108.0
C7-C8-C9	106.8 (4)	C1-C9-H9A	108.0
C7-C8-C11	106.0 (3)	C8-C9-H9B	108.0
C9-C8-C11	104.9 (5)	C1-C9-H9B	108.0
C1-C9-C8	116.9 (4)	H9A-C9-H9B	107.3
C1-C10-C5	111.9 (5)	C1-C10-H10A	109.2
C3-C11-C8	114.5 (6)	C5-C10-H10A	109.2
N6-C12-C13	126.3 (4)	C1-C10-H10B	109.2
C12-C13-C14	118.3 (5)	C5-C10-H10B	109.2
C12-C13-C15	121.0 (5)	H10A-C10-H10B	107.9
C14-C13-C15	120.6 (8)	C3-C11-H11A	108.6
C13-C14-C15i	119.6 (7)	C8-C11-H11A	108.6
C13-C15-C14i	119.8 (7)	C3-C11-H11B	108.6
C2-C1-H1	112.3	C8-C11-H11B	108.6
C10-C1-H1	112.3	H11A-C11-H11B	107.6
C9-C1-H1	112.3	N6-C12-H12	116.8
C1-C2-H2A	109.1	C13-C12-H12	116.8
C3-C2-H2A	109.1	C13-C14-H14	120.2
C1-C2-H2B	109.1	C15i-C14-H14	120.2
C3-C2-H2B	109.1	C13-C15-H15	120.1
H2A-C2-H2B	107.8	C14i-C15-H15	120.1
C4-C3-H3	110.5		

Table 4-Parameters of displacement (Å^2) for fractional atomic coordinates and isotropic or equivalent isotropic of the title compound

atoms	x	y	z	U_{iso}^*/U_{eq}
C1	0.1425 (5)	0.969 (3)	0.0600 (13)	0.05066*
C2	0.1416 (5)	0.766 (2)	-0.0039 (8)	0.05066*
C3	0.1552 (5)	0.575 (3)	0.0662 (13)	0.05066*
C4	0.1191 (4)	0.5625 (16)	0.1551 (11)	0.05066*
C5	0.1226 (4)	0.7559 (19)	0.2255 (10)	0.05066*
N6	0.0886 (4)	0.745 (2)	0.3131 (8)	0.05066*
C7	0.1726 (4)	0.785 (2)	0.2750 (9)	0.05066*
C8	0.2099 (6)	0.806 (2)	0.1884 (13)	0.05066*
C9	0.1935 (4)	0.9865 (18)	0.1138 (13)	0.05066*
C10	0.1091 (4)	0.9450 (17)	0.1539 (10)	0.05066*
C11	0.2049 (4)	0.6075 (19)	0.1181 (13)	0.05066*
C12	0.0661 (3)	0.571 (2)	0.3308 (8)	0.05066*
C13	0.0311 (4)	0.5325 (19)	0.4162 (9)	0.05066*
C14	0.0207 (5)	0.6963 (12)	0.4860 (10)	0.05066*
C15	0.0110 (4)	0.3373 (14)	0.4298 (8)	0.05066*
H1	0.1345	1.0894	0.0152	0.061*
H2A	0.1635	0.7769	-0.0618	0.061*
H2B	0.1101	0.7455	-0.0353	0.061*
H3	0.1544	0.4481	0.0231	0.061*
H4A	0.0874	0.5513	0.1236	0.061*
H4B	0.1252	0.4400	0.1984	0.061*
H7A	0.1805	0.6671	0.3203	0.061*
H7B	0.1732	0.9083	0.3194	0.061*
H8	0.2421	0.8256	0.2184	0.061*
H9A	0.2161	0.9992	0.0574	0.061*
H9B	0.1950	1.1139	0.1549	0.061*
H10A	0.0769	0.9282	0.1261	0.061*
H10B	0.1103	1.0700	0.1970	0.061*
H11A	0.2277	0.6146	0.0620	0.061*
H11B	0.2128	0.4877	0.1621	0.061*
H12	0.0725	0.4599	0.2859	0.061*
H14	0.0345	0.8258	0.4771	0.061*
H15	0.0183	0.2293	0.3839	0.061*

Conclusion

The research included a synthesis of new bis Schiff base which contains adamantyl moiety by condensation between two equivalents adamantan-1-ylamine and one equivalent of benzene-1,4-dicarbaldehyde in *n*-BuOH gave (1*E*,1'*E*)-1,1'-(1,4-phenylene)bis(*N*-(adamantan-1-yl)methanimine) with good yield. The skeleton of the compound was affirmed by FTIR, ^1H NMR, LC-MS spectroscopy, and X-ray powder diffraction techniques. The structure was solved by a parallel tempering process and refined by Rietveld refinement. The positions of two adamantan-1-ylimino groups are connected in the anti-conformation to the planar central 1,4-dimethylbenzene group. The rings of the adamantyl fragment showed that have a normal chair conformation.

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