INTRODUCTION

Schiff bases are condensation product of aliphatic or aromatic amines with carbonyl compounds (aldehydes or ketones) even in the absence of any catalyst (1, 2). The formation of Schiff bases usually takes place in an acidic condition, between the pH of 3 to 5 (3). The general formula of these compounds is RHC = N—R1, where R and R1 are alkyl, aryl, cycloalkyl, or heterocyclic groups (4). The Schiff base (also known as imines or azomethines). Azomethines employed in many fields such as paints, pigments, catalysis, organic semiconductors, cross-linked polymers, and corrosion inhibitors (5). Schiff base derived from aromatic aldehydes has arisen the researcher's interest because of its varied use in biological applications as anti-microbial (6), anti-fungal and anti-tumor activities (7, 8). O-vanillin is an optimal candidate for synthesizing various aromatic Schiff bases with important bioactivities. o-vanillin is a natural compound which has both phenolic OH and aldehyde group. Several reports are demonstrating that o-vanillin induces mutations and it has also been found to improve chromosomal aberrations in *in vitro* systems. Due to its numerous biological activities such as anti-inflammatory, analgesic and anti-viral activities, it is extensively studied in the medicinal field (9-11).

EXPERIMENTAL SECTION

Materials

All the chemicals and solvents used for the synthesis were of reagent grade. 1,5-di-amino-naphtalene (Acros), o-vaniline (Acros), ethanol, DMF and acetone used as received.

Procedure

Synthesis and crystallization

The title Schiff base ligand (Figure 1) was synthesized by refluxing the reaction mixture of hot ethanolic solutions (30 mL each) of 1,5-di-amino-naphtalene (0.01 mol) and o-vaniline (0.02 mol) for 2 h. The precipitates that formed during the reflux filtered and washed with cold ethanol. The purple crystals were grown in DMF-acetone (1:4) mixture by slow evaporation at room temperature for 2 weeks (yield 85%).

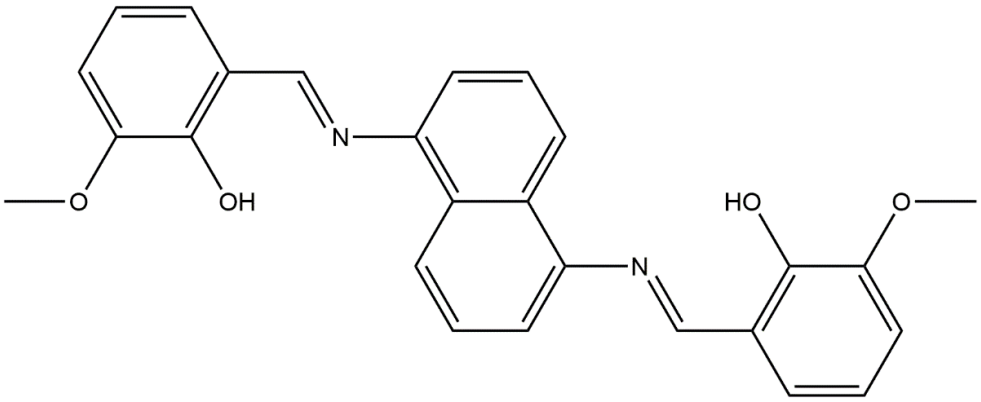


Fig. 1. The chemical structure of the Schiff base ligand.

X-ray structure determinations

The X-ray diffraction data collected on a Bruker APEX II using Mo Kα radiation. The *Apex2* (12) program package was used for cell refinements and data reductions. Multi-scan absorption correction (*SADABS*) (12) was applied to the intensities before structure solution. The structures solved by intrinsic phasing method using the *SHELXT* (13) software. Structural refinement carried out using *SHELXL-2017* (13). The crystallographic details were summarized in Table 1.

CCDC number 913117 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Computational details

The density functional theory (DFT) calculations were performed by using Gaussian 09W software program (14) using of Becke's three-parameter hybrid model with the Lee-Lang-Parr correlation functional (B3LYP) method with 6-31G(d,p) basis set.

Table 1. Crystallography experimental details.

Crystal data	
Chemical formula	$C_{26}H_{22}N_2O_4$
M_r	426.45
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293

***a*, *b*, *c* (Å)**	13.9984 (13), 5.1481 (5), 14.7277 (14)
β (°)	100.587 (2)
***V* (Å³)**	1043.29 (17)
Z	2
Radiation type	Mo *K*α
μ (mm⁻¹)	0.09
Crystal size (mm)	0.25 × 0.22 × 0.14

Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.817, 0.966
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10769, 3025, 2065
R_{int}	0.028
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.704

Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.147, 1.06
No. of reflections	3025
No. of parameters	150
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.16

RESULTS AND DISCUSSION

Crystal description

The title centrosymmetric compound, [$C_{26}H_{22}N_2O_4$], crystallizes in the monoclinic space group P 21/c with Z = 2. In the molecule, an intra-molecular O1—H1O1···N1 hydrogen bond generates an S(6) ring (Figure 2 and Figure 3; Table 2). The dihedral angle between the o-Vanillin

ring and 1,5-Di-amino-naphthalene ring is 19.05 (7)°. The torsion angle C8/N1/C7/C6 which connected o-Vanillin and 1,5-Di-amino-naphthalene rings is 177.37 (13)°. The Schiff base C7═N1 bond length 1.2794 (18) Å is almost exactly equal to the typical C═N bond length of uncomplexed Schiff bases (15).

The O-bound H atoms were located in a difference Fourier map and were refined freely. The remaining H atoms were positioned geometrically and refined using a riding model with C–H = 0.93–0.96 or 1.00 Å and Uiso(H) = 1.2Ueq(C) for aromatic and Uiso(H) = 1.5Ueq(C) for methyl group.

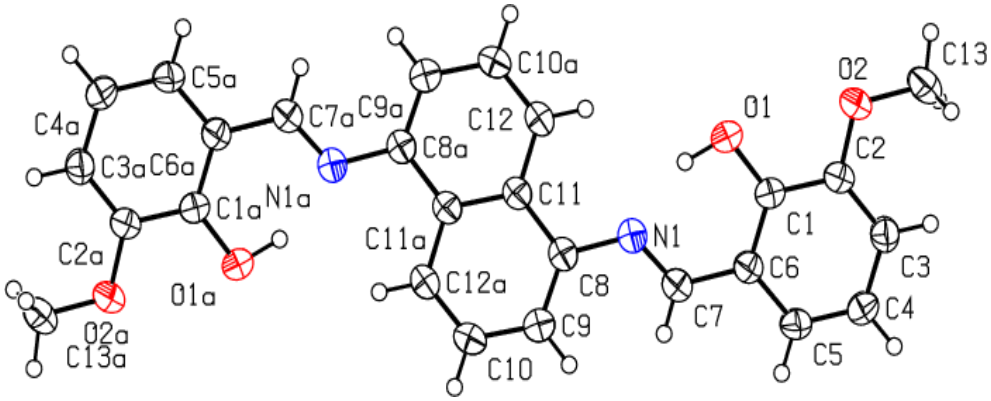


Fig. 2. A view of the structure of the Schiff base, showing the atom-labelling scheme.

Displacement ellipsoids were drawn at the 50% probability level. Symmetry code: (*a*) − *x*, −*y*, 1 − *z*.

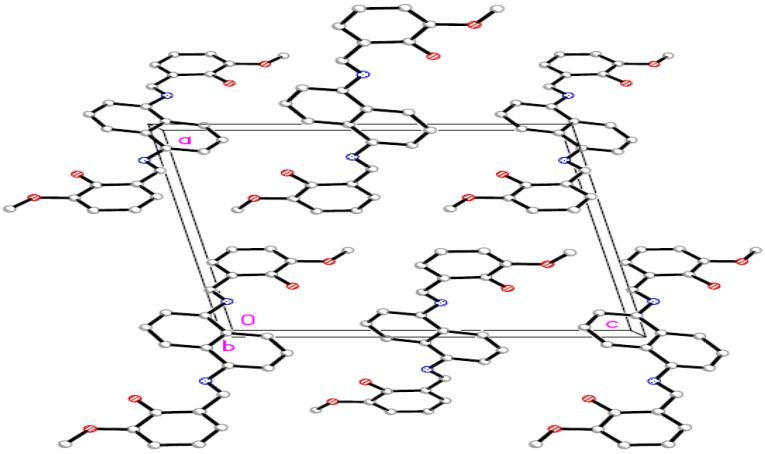


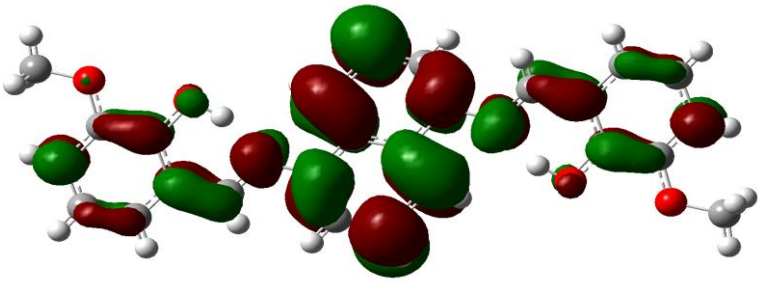
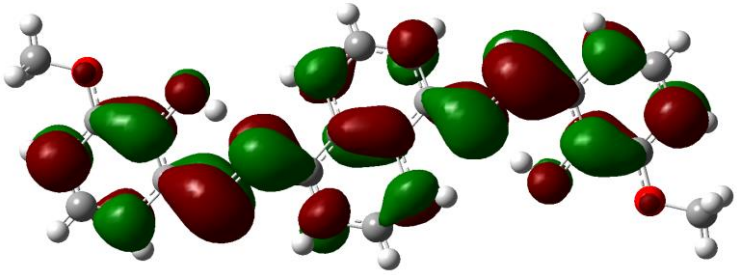
Fig. 3. The crystal packing of the title compound viewed down b axis.

Table 2. Hydrogen-bond geometry (Å, º)

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O1—H1*O*1···N1	0.95 (2)	1.70 (2)	2.5941 (16)	157 (2)

Molecular orbital analysis

Frontier molecular orbitals have a crucial role in the chemical stability, optical properties and biological activities of the molecules. Among these, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the most important. Figure 4, showed the electron density of the HOMO–2, HOMO–1, HOMO, LUMO, LUMO+1, and LUMO+2 molecular orbitals. Analysis of these orbitals showed that these orbitals are mainly composed of benzene and naphthalene rings. The composition of each fragment is shown in Table 3.

LUMO+2	
LUMO+1	

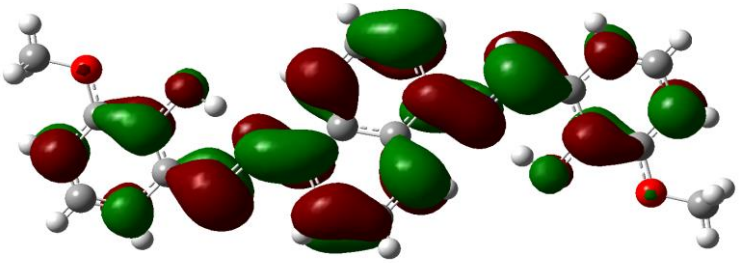
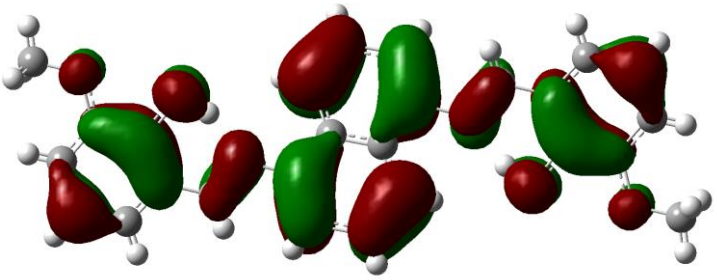
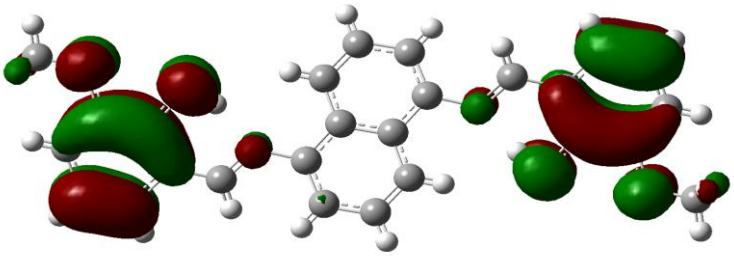
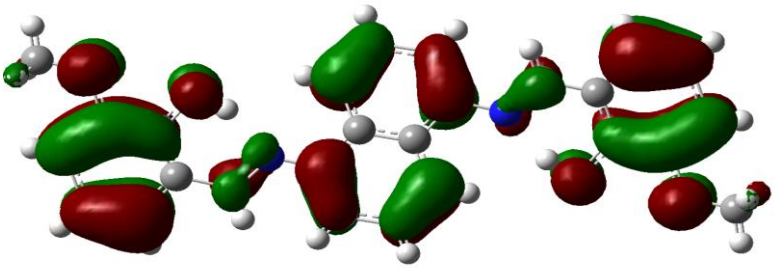
LUMO	
HOMO	
HOMO-1	
HOMO-2	

Fig. 4. Molecular orbital shapes using B3LYP/6-31G**.**

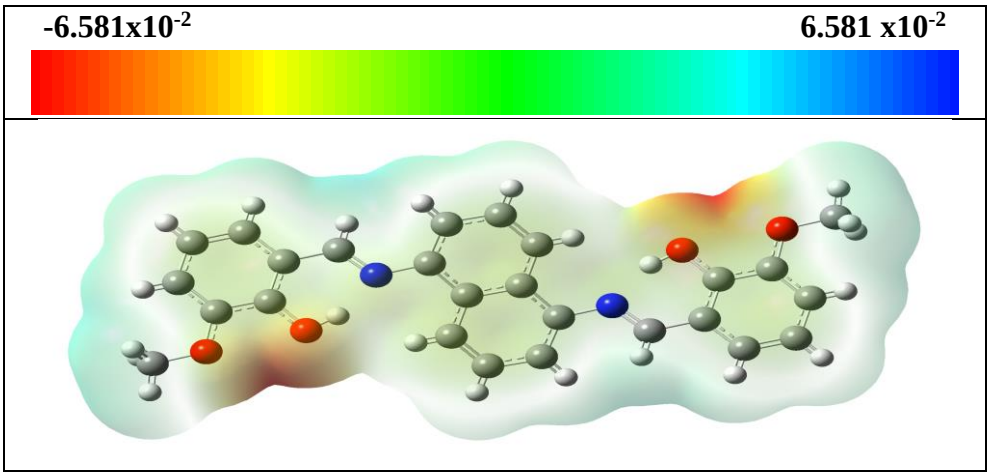
Table 3. Molecular orbital composition.

MO	Benzene ring A*	Benzene ring B*	naphthanlene	Methoxy group A*	Methoxy group B*	Hydroxy group A*	Hydroxy group B*	Azomethine group A*	Azomethine group B*
L+2	0.14	0.14	0.45	-	-	0.06	0.06	0.06	0.06
L+1	0.07	0.07	0.70	-	-	-	-	0.07	0.07
LUMO	0.14	0.14	0.22	-	-	-	-	0.23	0.23
HOMO	0.10	0.10	0.42	-	-	-	-	0.17	0.17
H-1	0.14	0.14	0.45	-	-	0.06	0.06	0.06	0.06
H-2	0.26	0.27	0.05	0.10	0.10	0.09	-	-	-

*** A for groups on the left-hand side and B for the group on the right-hand side in the molecule**

Molecular electrostatic potential

Molecular electrostatic potential (MEP) is used to investigate the nucleophilic or electrophilic regions in a molecule. The surface of the title compound shown in Figure 5. The most negative (red) regions observed around the oxygen atoms showing nucleophilic reactivity.



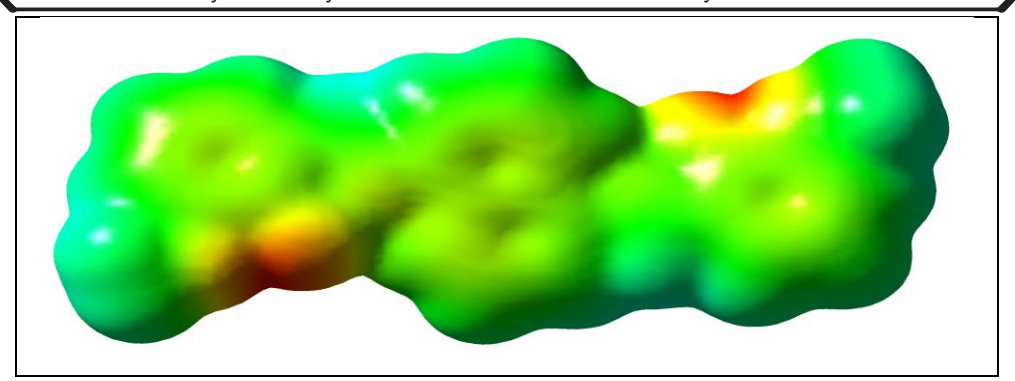


Fig. 5. Molecular electrostatic potential map.

CONCLUSION

The compound 6,6'-((1E,1'*E*)-(naphthalene-1,5-diylbis(azaneylylidene))bis(methaneylylidene))bis(2-methoxyphenol) (NaphVan) was synthesized and characterized using XRD single crystal. DFT calculations performed to analysis the molecular orbitals and MEP.

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