
STRUCTURE OF ORGANIC
COMPOUNDS

Synthesis, Molecular Structure and Spectroscopic Studies of 6,6'-(1*E*,1'*E*)-(Ethane-1,2-Diylbis(azan-1-yl-1-ylidene))bis(phenylmethan-1-yl-1-ylidene)bis(3-(Octyloxy)phenol)

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Received May 6, 2019; revised December 17, 2019; accepted December 19, 2019

Abstract—6,6'-(1*E*,1'*E*)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(phenylmethan-1-yl-1-ylidene)bis(3-(octyloxy)phenol) has been synthesized and characterized by FTIR, ¹H, ¹³C NMR and single-crystal X-ray determination. The compound crystallizes in monoclinic space group *C2/c* with *Z* = 4 in the unit cell. The asymmetric unit of the compound contains one half-organic molecule. The molecule is located about a two-fold rotation axis which bisects the central C14-C14ⁱ bond. The dihedral angle between the phenyl rings is 68.46(11)°. In the crystal, intramolecular O—H⋯N hydrogen bonds generates a six-membered ring, producing an S(6) ring motif. The crystal packing is also stabilized by C—H⋯π interactions.

DOI: 10.1134/S1063774520070251

INTRODUCTION

Schiff bases and its derivatives are an important class of compounds which can be used in a variety of studies such as organic synthesis, catalysis, drug design, industry and the life sciences [1–3]. Schiff bases have received much attention because of their potential applications with some of these compounds

exhibiting various pharmacological activities such as anticancer, anti-HIV, antibacterial and antifungal properties [4–7]. On the industrial scale, they have a wide range of applications, such as in dyes and pigments [8].

Due to the biological and industrial significance of the Schiff bases, we have synthesised derivatives of Schiff base, 6,6'-(1*E*,1'*E*)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(phenylmethan-1-yl-1-ylidene)bis(3-(octyloxy)phenol) (Fig. 1), for the first time. In this study, we present the structure of 6,6'-(1*E*,1'*E*)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(phenylmethan-1-yl-1-ylidene)bis(3-(octyloxy)phenol) was studied by using FTIR, ¹H NMR, ¹³C NMR, and X-ray crystallographic techniques.

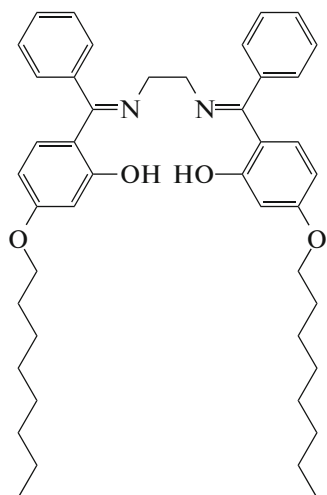


Fig. 1. Chemical diagram of 6,6'-(1*E*,1'*E*)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(phenylmethan-1-yl-1-ylidene)bis(3-(octyloxy)phenol).

EXPERIMENTAL

Synthesis

6,6'-(1*E*,1'*E*)-(Ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(phenylmethan-1-yl-1-ylidene)bis(3-(octyloxy)phenol) was prepared by refluxing a mixture of a solution containing 2-hydroxy-4-octyloxybenzophenone (10.4 mg, 0.07 mmol) in tetrahydrofuran (THF) (20 mL) and a solution containing 1,2-ethylene-diamine (18.0 mg, 0.07 mmol) in THF (20 mL). The reaction mixture was stirred for 5 h under reflux. The obtained crystal material was yellow and washed with ethanol, dried at room temperature (m.p. 379–381 K).

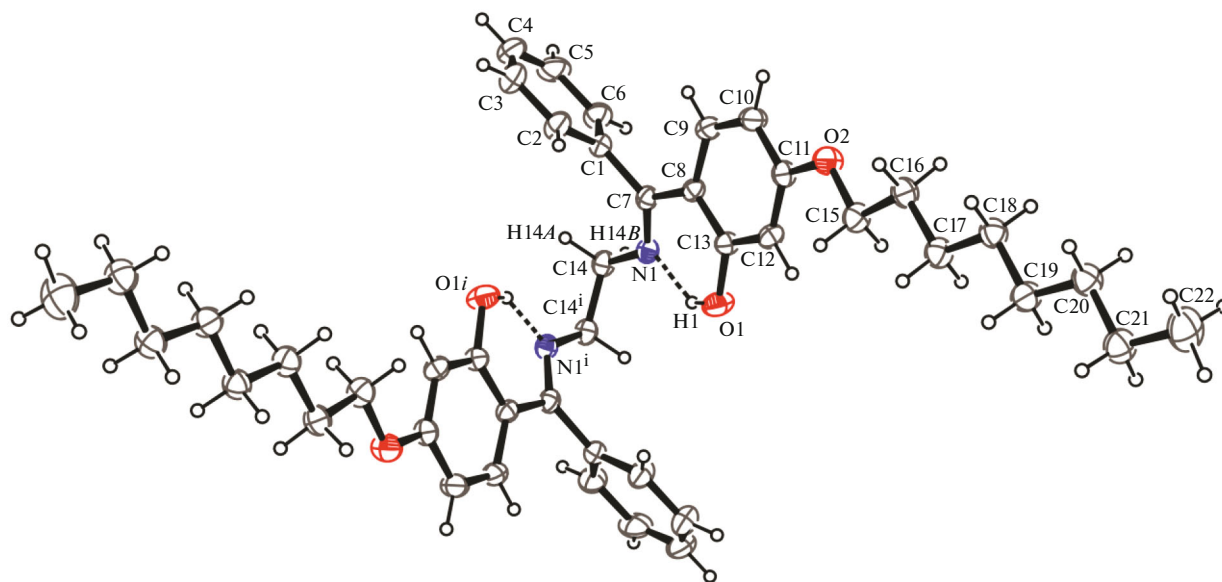


Fig. 2. Ortep-3 diagram of the 6,6'-(1*E*,1'*E*)-(ethane-1,2-diybis(azan-1-yl-1-ylidene))bis(phenylmethan-1-yl-1-ylidene)bis(3-(octyloxy)phenol). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bonds are shown as dashed lines.

Spectral Studies

The IR spectrum of the title compound was recorded in the range 4000–400 cm^{-1} using a Vertex 80V Bruker FTIR spectrophotometer. ^1H - and ^{13}C -NMR spectra were obtained on a Bruker Ultra Shield Plus 500 MHz spectrometers using TMS as internal standard. The spectra were recorded in DMSO solutions.

Crystal Data and Structure Determination

All diffraction measurements were performed at room temperature (296 K) using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a BRUKER APEX II diffractometer. Reflections were collected in the rotation mode and cell parameters were determined by using Bruker SAINT software [9]. Absorption correction was achieved by the integration method via Bruker SAINT software [9]. The structure was solved by direct methods using SHELXS 97 [10]. H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.82, 0.93, 0.96, and 0.97 \AA for OH, CH, CH_3 , and CH_2 atoms, respectively. The ORTEP-3 program for windows has been used in the preparation of the figures [11]. The crystallographic data and refinement parameters for the structural analyses are as follows: $\text{C}_{44}\text{H}_{56}\text{N}_2\text{O}_4$, $M_r = 676.91$, prism and colourless, size $0.12 \times 0.15 \times 0.17 \text{ mm}$, space group $C2/c$, monoclinic, $a = 33.750 (4) \text{ \AA}$, $b = 6.4978 (6) \text{ \AA}$, $c = 18.070 (2) \text{ \AA}$, $\beta = 100.248 (5)^\circ$, $V = 3899.7 (7) \text{ \AA}^3$, $Z = 4$, $D_x = 1.153 \text{ Mg m}^{-3}$, $\mu = 0.07 \text{ mm}^{-1}$, $3^\circ \leq \theta \leq 26^\circ$, measured reflections = 15085, reflections with $I > 2\sigma(I) = 1846$,

$R_{\text{int}} = 0.093$, $GOF = 1.00$, $R_1 (I > 2\sigma(I)) = 0.0549$, $wR_2 (I > 2\sigma(I)) = 0.134$, number of refined parameters = 234, $-41 \leq h \leq 41$, $-8 \leq k \leq 8$, $-22 \leq l \leq 22$, $T_{\text{min}}/T_{\text{max}} = 0.8592/0.9842$, $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.15/-0.18 \text{ e/\AA}^3$.

Crystallographic data for the structural analysis have been deposited with Cambridge Crystallographic Data Centre, CCDC reference number 1813286. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB12 1EZ, UK. Fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

Crystal Structure

The title compound, an Ortep-3 view of which is shown in Fig. 2, crystallizes in the monoclinic space group $C2/c$ with $Z = 4$. The asymmetric unit of the title compound, $\text{C}_{44}\text{H}_{56}\text{N}_2\text{O}_4$, contains one half-organic molecule. The molecule is located about a two-fold rotation axis which bisects the central C14–C14ⁱ bond (symmetry code (i): $-x + 1, y, -z + 1/2$). The title compound is not planar. The dihedral angle between the C1/C6 and C8/C13 rings is $68.46(11)^\circ$. The torsion angle of the bridge N–CH₂–CH₂–N group is 68.64° . The length of the C7=N1 double bond is $1.286 (2) \text{ \AA}$, it is slightly longer than standard 1.28 \AA value of C=N double bond and consistent with the related structures [12, 13]. The selected bond lengths and bond angles are given in Table 1. In the molecule, the bond lengths and angles are within normal ranges

Table 1. Selected molecular structure parameters

Atoms	Experiment	Atoms	Experiment
Bond lengths, Å			
C14–C14 ⁱ	1.498 (4)	C16–C15	1.501 (3)
O1–C13	1.348 (2)	C16–C17	1.509 (3)
N1–C7	1.286 (2)	C17–C18	1.513 (3)
N1–C14	1.460 (3)	C19–C18	1.508 (3)
O2–C11	1.359 (2)	C19–C20	1.512 (3)
O2–C15	1.426 (2)	C20–C21	1.510 (3)
Bond angles, deg			
C7–N1–C14	122.75 (18)	O2–C11–C12	124.2 (2)
O1–C13–C12	117.16 (19)	O2–C11–C10	115.7 (2)
O1–C13–C8	121.61 (19)	N1–C7–C8	118.11 (19)
C11–O2–C15	117.57 (16)	N1–C7–C1	123.74 (19)
N1–C14–C14 ⁱ	109.67 (17)	O2–C15–C16	109.39 (18)
C15–C16–C17	111.14 (19)	C18–C19–C20	115.27 (19)
C16–C17–C18	115.1 (2)	C21–C20–C19	114.3 (2)
Torsion angles, deg			
O1–C13–C8–C9	–177.48 (19)	C9–C8–C7–N1	163.38 (19)
O1–C13–C8–C7	1.8 (3)	C13–C8–C7–N1	–15.9 (3)
C7–N1–C14–C14 ⁱ	–143.9 (2)	O2–C11–C10–C9	–178.23 (19)
C15–O2–C11–C12	–7.2 (3)	C11–O2–C15–C16	–179.27 (17)
C15–O2–C11–C10	173.27 (18)	C17–C16–C15–O2	–178.78 (18)
C14–N1–C7–C8	178.38 (18)	C6–C1–C7–N1	118.2 (2)
C14–N1–C7–C1	0.9 (3)	C2–C1–C7–N1	–60.7 (3)
O1–C13–C12–C11	178.22 (19)	O2–C11–C12–C13	–179.77 (18)

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

and they are comparable with those related structures [14–16].

The intramolecular O–H \cdots N hydrogen bonds (Fig. 2) generates a six-membered ring, producing an S(6) ring motif [17]. The crystal structure is also stabilized by intermolecular C–H \cdots π interactions (C16–H16A \cdots Cg2 with symmetry code: $x, 1 + y, z$). Cg2 is the centroids of the C8–C13 ring. The details of the hydrogen bonds are summarized in Table 2. A packing diagram of the title compound is shown in Fig. 3.

IR Spectra

The infrared spectra of the title compound were recorded in Vertex 80V Bruker FTIR spectrometer using KBr pellets in the region of 4000–400 cm^{-1} . The IR spectra contain some characteristic bands of the stretching vibrations of the O–H, C–H, C=N, C=C, and C–O groups. The broad band at 3441 cm^{-1} was assigned phenol OH stretching vibrations. The C–H aromatic stretchings were observed at 3027 cm^{-1} . Besides, the stretching of imine C–H was found at 2920 cm^{-1} . The strong band at 1601 cm^{-1} was assigned

to azomethine C=N stretching vibration. The band at 1511 cm^{-1} is assigned to C=C stretchings. The C–O stretching band is observed at 1261 cm^{-1} . The above conclusions are in good agreement with the related Schiff base compound [18–20].

NMR Spectra

^1H chemical shift values of the title compound are observed to be 0.83–7.50 ppm. The aromatic C–H signals were observed to be 6.16–7.50 ppm. The OH proton is observed 3.92 ppm singlet. The $-\text{NCH}_2$ and $-\text{OCH}_2$ protons resonate at 3.45 and 3.30 ppm. The signals at 0.83–2.48 ppm are due to CH_2 and CH_3 protons.

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

D–H \cdots A ^a	D–H	H \cdots A	D \cdots A	D–H \cdots A
O1–H1 \cdots N1	0.82	1.85	2.569(2)	146
C16–H16A \cdots Cg2 ⁱ	0.97	2.98	3.775(2)	140

^a Symmetry code: (i) $x, 1 + y, z$.

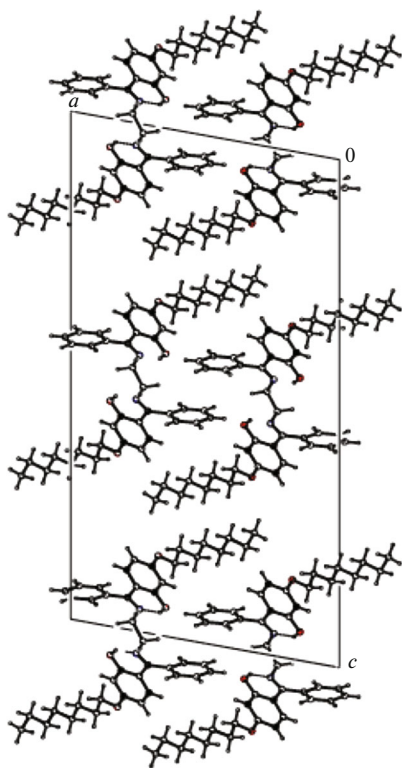


Fig. 3. Packing diagram of 6,6'-(1*E*,1'*E*)-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(phenylmethan-1-yl-1-ylidene)bis(3-(octyloxy)phenol).

^{13}C NMR spectra of the compound show signal at 169.00 ppm due to the carbon C7 atom of the C=N group. The chemical shift value of C13 atom bounded the OH group is observed as 163.20 ppm. While the C14 atom of the $-\text{NCH}_2$ group gave a singlet at 67.84 ppm, the carbons of the CH_2 and CH_3 groups are observed at 14.27–31.54 ppm. The aromatic carbons of phenyl ring are observed at 127.47–133.41 ppm. The ^1H and ^{13}C NMR spectra are in agreement with the X-ray structure of the title compound.

CONCLUSIONS

6,6'-(1*E*,1'*E*)-(Ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(phenylmethan-1-yl-1-ylidene)bis(3-(octyloxy)phenol) has been synthesized and characterized by FT-IR, ^1H NMR, ^{13}C NMR, and single-crystal X-ray diffraction analysis. The structure was unambiguously assigned by X-ray diffraction studies. The FT-IR and NMR spectroscopy and single crystal structure data confirm that the state of the ligand in

solution and in the solid state corresponds to one form. In the crystal structure of the title compound, the intramolecular O–H \cdots N hydrogen bonds generates a six-membered ring, producing an S(6) ring motif. The crystal structure is also stabilized by intermolecular C–H \cdots π interactions.

FUNDING

This study was supported financially by the Research Centre of Ondokuz Mayıs University (project no. PYO.FEN.1904.18.003).

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