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Synthesis, Characterization and Crystal structure of Chiral Schiff base compound (*E*)-3, 4-Dimethoxy [(1-phenylethyl) iminomethyl] benzyne

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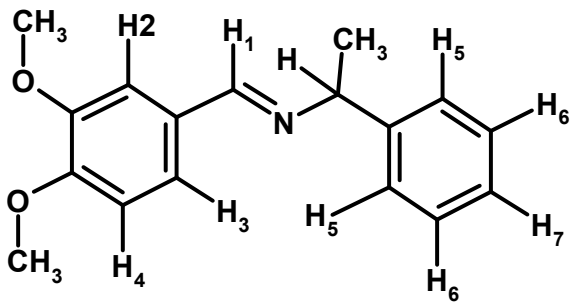
Abstract: The crystal structure of the title chiral Schiff base compound (*E*)-3,4-dimethoxy[(1-phenylethyl)iminomethyl]bezyne (**1**) was determined by single-crystal X-ray diffraction data. The title compound was further characterized by elemental analyses (CHN), FT-IR, ^{1}H-NMR and UV-Vis spectroscopic techniques. It crystallizes in the monoclinic space group $P2_1$ with unit cell parameters: a = 19.0121 (2), b = 8.2507 (2), c = 9.7331 (4) Å, β = 92.488 (2)°, V = 1525.33 (7) Å^3, Z = 4, R_1 = 0.0299, wR_2 = 0.787, R_1 = 0.0329, wR_2 = 0.0804.

Keywords: *Chiral Schiff-base; crystal structure; spectroscopy; monoclinic.*

Introduction

Schiff-bases have been used extensively as ligands in the field of coordination chemistry and they have interesting structures [1-3]. These compounds have been synthesized by condensation of carbonyl compounds with amines [4,5]. Furthermore, free Schiff base compounds may have antimicrobial [6] and nonlinear optical [7] properties. They may exhibit photochromism and thermochromism in the solid state by proton transfer [8] and they may act as anion sensor [9]. Several groups have developed chiral Schiff base ligands and theirs transition metal complexes [10-14].

As an additional contribution to the synthesis, characterization and crystal structures of Schiff-base compounds and theirs transition metal complexes and in the course of our ongoing studies of these kinds of materials [15-20], in this work,, we report on synthesis, characterization and crystal structure of a new chiral Schiff base compound (*E*)-3,4-dimethoxy[(1-phenylethyl) iminomethyl] benzyne (Scheme 1).



Scheme 1 The chemical structure of (E)-3,4-dimethoxy[(1-phenylethyl)iminomethyl]bezyne.

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Experimental

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purification. Infrared spectra were recorded using KBr disks on a FT-IR Perkin–Elmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. ^{1}H-NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. All chemical shifts are reported in δ units downfield from TMS. Thermogravimetric analyses were done on a Perkin Elmer TGA/DTA lab system 1 (Technology by SII) in nitrogen atmosphere with a heating rate of 20ºC/min from 35 to 700 ºC. UV–Vis absorption spectra were recorded on a JASCO V-570 spectrophotometer; $\lambda_{max}/\varepsilon$ in nm.

Synthesis of (E)-3,4-dimethoxy[(1-phenylethyl) iminomethyl] benzyne

3,4-Dimethoxybenzaldehyde (0.4 mmol) and 1-phenylethylamine (0.4 mmol) were dissolved in a mixture of methanol:chloroform (1:1 *v/v*, 20 ml) at room temperature. The mixture was stirred and heated for 30 min to give a clear solution. After cooling, the product was allowed to crystallize at room temperature. Colorless crystals were formed at the bottom of the vessel after 5 days of slow evaporation of the solvent. The resulting colorless crystals were collected by filtration and dried at room temperature. Yield: 80%. *Anal*. Calc. for $C_{17}H_{19}NO_2$: C, 75.80; H, 7.11; N, 5.20%. Found: C, 75.92; H, 7.25; N, 5.24%. IR (KBr pellet, cm^{-1}): 2924-3079 (CH aliphatic and aromatic), 2842 (s, -CH=N-); 1641 (s, C=N). UV–Vis, λ_{max} (nm)/ε ($M^{-1}cm^{-1}$); 269 (19971), 301 (13603), 355 (1273). ^{1}H-NMR ($CDCl_3$, δ(ppm)): 1.61 (d, 3H, -N-HC-C**H**$_3$), 3.91 (s, 3H, -OC**H**$_3$), 3.96 (s, 3H, -OC**H**$_3$), 4.54 (q, 1H, -C**H**-N-), 6.87 (d, 1H, **H**$_4$), 7.19 (dd, 1H, **H**$_3$), 7.25 (t, 2H, **H**$_7$), 7.35 (3, 2H, **H**$_6$), 7.44 (d, 2H, **H**$_5$), 7.51 (s, 1H, **H**$_2$), 8.29 (s, 1H, **H**$_1$).

X-ray crystallography

A single crystal of **1** was chosen for X-ray diffraction study. Crystallographic measurements were done at 150 K with four circle CCD diffractometer Gemini of Oxford Diffraction, Ltd., with mirrors-collimated Cu *K*α radiation (λ = 1.54184 Å). The crystal structure was solved by direct methods with program SIR2002 [21] and refined with the Jana2006 program package [22] by full-matrix least-squares technique on F^2. The molecular structure plots were prepared by ORTEP III [23]. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice they were nevertheless kept in ideal positions during the refinement. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as $1.2U_{eq}$ of the parent atom. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1. Selected bond distances and angles are given in Table 2.

Table 1. Crystallographic data, collection and parameters of structure refinement

Chemical formula	$C_{17}H_{19}NO_2$
Formula weight	269.3
Crystal system	Monoclinic
Space group	$P2_1$
Z	4
T (K)	150
a, Å	19.0121(2)
b, Å	8.2507(2)
c, Å	9.7331(4)
β, deg	92.488(2)
V, Å^3	1525.33(7)
T_{min}	0.178
T_{max}	1.000
μ, mm^{-1}	0.61
Measured reflections	31335
Independent reflections	2900
Reflection with $I > 3\sigma(I)$	2665
R_{int}	0.041
S	1.85
$R[F^2>3\sigma(F^2)]$	0.030
$wR(F^2)$	0.080
Parameters	360
$\Delta\rho_{max}$, eÅ^{-3}	0.09
$\Delta\rho_{min}$, eÅ^{-3}	-0.10
Crystal size, mm^3	0.52 × 0.39 × 0.08

Table 2 Selected interatomic distances (Å) and bond angles (°).

O1-C4	1.370(2)	O3-C21	1.366(2)
O1-C8	1.414(3)	O3-C25	1.421(3)
O2-C5	1.363(2)	O4-C22	1.360(2)
O2-C9	1.424(3)	O4-C26	1.428(2)
N1-C1	1.259(3)	N2-C18	1.258(3)
N1-C10	1.468(2)	N2-C27	1.470(2)
C4-O1-C8	116.99(16)	C21-O3-C25	116.70(14)
C5-O2-C9	117.94(17)	C22-O4-C26	117.18(16)
C1-N1-C10	117.93(18)	C18-N2-C27	116.53(19)
N1-C1-C2	123.25(19)	N2-C18-C19	124.0(2)
N1-C10-C11	110.0(2)	N2-C27-C28	109.44(16)
N1-C10-C17	108.67(19)	N2-C27-C34	108.9(2)
O1-C4-C3	125.11(18)	O3-C21-C20	125.03(18)
O1-C4-C5	114.58(15)	O3-C21-C22	114.63(14)
O2-C5-C4	115.02(17)	O4-C22-C21	115.39(17)
O2-C5-C6	125.37(18)	O4-C22-C23	124.97(17)

Results and discussion

The title compound was obtained in relatively high yield, 89%. The stability of dissolved compound is much shorter than in the solid state and depends on the nature of the solvent. The title compound is stable in methanol and acetonitrile solution at room temperature for several days, and it remains unchanged in chloroform and dichloromethane for about one week at room temperature.

Spectral characterization

The observed strong bands at 2842 and 1641 cm^{-1} in FT-IR spectrum are assigned to the –CH=N- and -C=N- stretching vibrations [15-20]. The FT-IR spectraum also shows several weak bands corresponding to aromatic and aliphatic C-H stretching (2924-3079 cm^{-1}), and aromatic C-C stretching (1419-1600 cm^{-1}) [15-20].

The electronic spectrum of the synthesized compound has been recorded by using the spectrometer in the range of 200-600 nm. The representative UV-Vis spectrum of the title compound in chloroform is shown in Fig 1. As seen in the spectrum, there is no absorption in the visible region of the studied compound. All absorption bands of the title compound can be assigned to π-π* and n-π* transitions of phenyl ring, C=N and MeO- groups.

The 1H-NMR spectrum of the title compound displays one singlet signal at 1.60 ppm, two singlet signals at 3.91 and 3.96 ppm, , one singlet signal at 4.53 ppm, and one singlet signal at 8.29 ppm, assigned to protons of CH3-C group, CH3O- groups, C-CH-Ph group and -HC=N group, respectively (Fig. 2). Hydrogens of aromatic rings appear between 6.87 – 7.51 ppm.

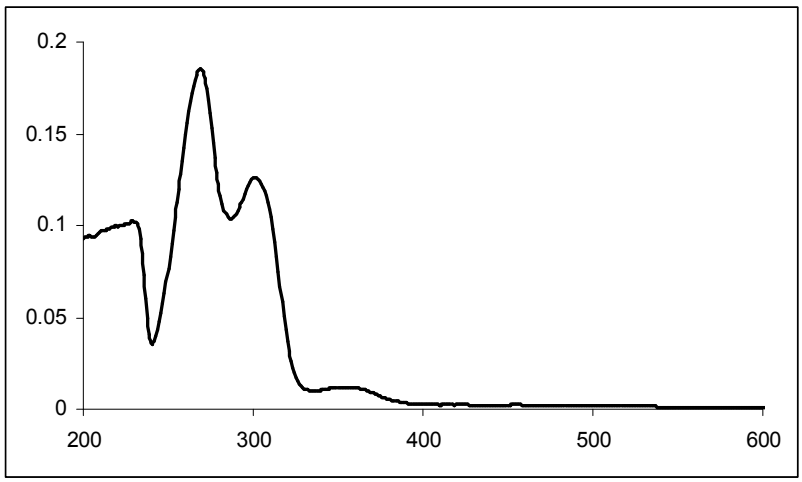

Fig 1. UV-Vis absorption spectrum of the title compound in chloroform.

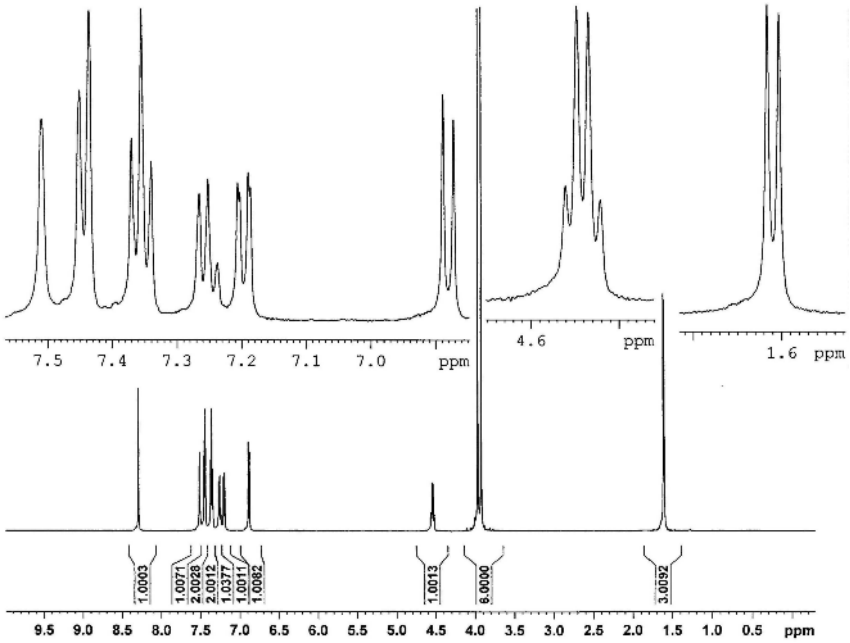

Fig. 2 1H-NMR spectrum of the title compound in CDCl3.

Crystal structure description

The title compound crystallizes in the monoclinic space group $P2_1$, with two independent molecules in the asymmetric unit. The molecular structure of the title compound with the atom numbering scheme is given in Fig. 3. All bond distances and angles are normal and are in good agreement with those reported in similar Schiff-base compounds [15-20].The C1 ═ N1 and N2=C18 bond lengths of 1.259(3) and 1.258(3) Å, respectively, conform to the value for a double bond, while the N1-C10 and N2-C27 bond lengths of 1.468(2) and 1.470(2) Å, respectively, conform to the value for a single bond, like in similar Schiff-base compounds [18-28]. The bond angles the C1=N1-C10 and C18=N2-C27 bond angles are 117.93(18) and 116.53(19)º, respectively, which is consistent with the sp^2 hybrid character of N1 and N2 atoms. There is difference in planarity in the two symmetry independent molecules, because the torsion angles of C18-N2-C27-C28 (112.07º) and C4-N1-C10-C11 (133.18º) are different (Fig. 4). The molecular conformation is stabilized by an intermolecular C7-H7···O4 hydrogen bond (Fig. 3 and Table 3).

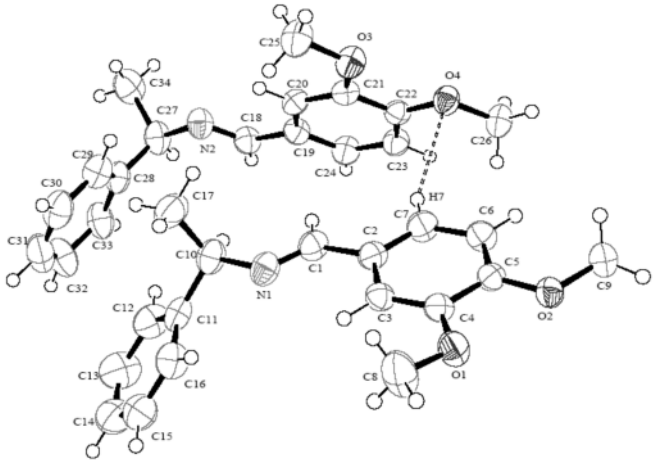

Fig. 3 The molecular structure of the title compound in 50% probability ellipsoids. H atoms are shown as spheres of arbitrary radii. The dashed line presents a hydrogen bond.

Table 3 Hydrogen-bond geometry (Å, °).

D-H···A	*D*-H	H···*A*	*D*···*A*	*D*-H···*A*
C7—H7···O4	0.960	2.582	3.415(2)	145.216

Conclusion

In summary, new chiral Schiff-base compound (*E*)-3,4-dimethoxy[(1-phenylethyl)iminomethyl] benzyne derived from 3,4-dimethoxybenzaldehyde and 1-phenylethylamine was synthesized and characterized. Crystal structure of the title compound was successfully determined by single-crystal X-ray diffraction. Elemental analyses confirms the chemical composition of the synthesized compound while FT-IR, UV-vis and ^{1}H-NMR spectroscopy confirms the functional groups, particularly -HC=N imine groups, of the compound.

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 761896. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or http:www.ccdc.cam.ac.uk.

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