

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURES OF NOVEL BIS-NO-ACYCLIC SCHIFF BASE COMPOUNDS

A. D. Khalaji¹, K. Fejfarova², M. Dušek²

¹Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran
E-mail: alidkhalaji@yahoo.com

²Institute of Physics of the ASCR, Prague, Czech Republic

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Novel bis-NO-acyclic Schiff base compounds are synthesized by the condensation of 3-methoxy-4-(2-(4-formyl-2-ethoxyphenoxy)ethoxy)benzaldehyde with 2-aminophenol (**L**¹) or 4-aminophenol (**L**²). The titled compounds with the monoclinic space group *C2/c* are characterized by elemental analyses and single crystal X-ray diffraction.

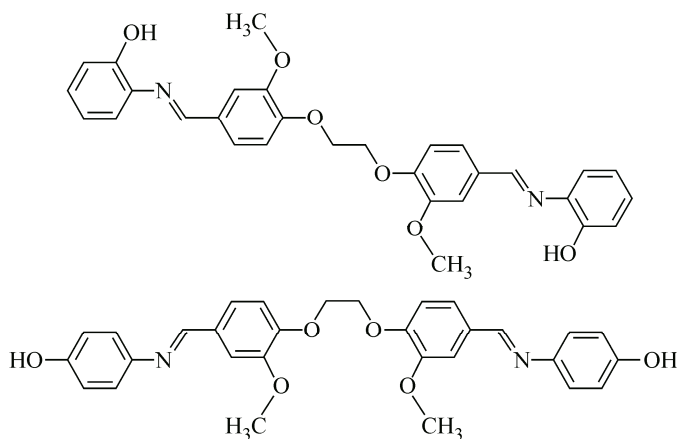
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A Schiff base, named after Hugo Schiff, is formed by the condensation of an amine group with the carbonyl group of an aldehyde or ketone. The mechanism of this reaction consists of the nucleophilic addition of the amine group to the carbonyl one, forming a hemiaminal, followed by a dehydration to generate an imine of the general formula $R_3R_2C=NR_1$ [1–4]. Schiff bases can be used as ligands in coordination chemistry because of the basic character of π -acceptor properties of the imine nitrogen atom [5–8]. The physical properties and reactivity of imines have been studied for more than a hundred years [9–11]. Furthermore, they are reported to show a variety of biological activities, including antibacterial, antifungal, anticancer, and herbicidal effects [12]. In recent year, various groups reported the inhibition effect of Schiff bases on steel and iron corrosion [13–16]. Recently, Khalil and co-workers have synthesized a new Schiff base derived from sulfanilamide that shows a reproducible change in its color due to the addition of acid and base and that can be used as an acid-base indicator [17]. Dalapati and co-workers report an anion receptor based on a Schiff base compound derived from *o*-phenylenediamine and 5-nitro-salicylaldehyde, which can selectively detect F^- and AcO^- ions by a naked-eye visible color change (colorless to yellow) [18]. In 2009 Hijji and co-workers reported a Schiff base as a calorimetric anion sensor which showed a selective coloration for F^- , AcO^- , $H_2PO_4^-$ in acetonitrile and was selective to acetate in aqueous acetonitrile [19].

Recently, our group has reported the syntheses and crystal structures of Schiff base compounds [4, 20–25]. Herein, we report the synthesis and the crystal structure determination of novel bis-NO-acyclic Schiff base compounds, derived from 3-methoxy-4-(2-(4-formyl-2-ethoxyphenoxy)ethoxy)benzaldehyde with 2-aminophenol (**L**¹) or 4-aminophenol (**L**²) (Scheme 1).

Experimental. Materials and instruments. All reagents and solvents for the synthesis and analysis were commercially available and used as received without further purifications. 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. 3-Methoxy-4-(2-(4-formyl-2-ethoxyphenoxy)ethoxy)benzaldehyde was prepared following the literature procedure [26].

Scheme 1. Chemical structures of L^1 and L^2

Synthesis of L^1 . 3-Methoxy-4-(2-(4-formyl-2-ethoxyphenoxy)ethoxy)benzaldehyde (0.2 mmol) and 2-aminophenol (0.2 mmol) were dissolved in methanol at room temperature. The mixture was stirred and heated for 60 min to give a clear solution. The mixture was cooled and allowed to crystallize at room temperature. After keeping the solution in air for 4 days by slow evaporation of the solvent, pale yellow crystals formed at the bottom of the vessel. The resulting crystals were collected by filtration and dried at room temperature. Yield: 65%. *Anal.* Calc. for $C_{30}H_{28}N_2O_6$: C 70.30, H 5.51, N 5.47%. Found: C 70.35, H 5.56, N 5.51%.

Synthesis of L^2 . 3-Methoxy-4-(2-(4-formyl-2-ethoxyphenoxy)ethoxy)benzaldehyde (0.2 mmol) and 4-aminophenol (0.2 mmol) were dissolved in methanol at room temperature. The mixture was stirred and heated for 60 min to give a clear solution. The mixture was cooled and allowed to crystallize at room temperature. After keeping the solution in air for four days by slow evaporation of the solvent, pale yellow crystals formed at the bottom of the vessel. The resulting crystals were collected by filtration and dried at room temperature. Yield: 65%. *Anal.* Calc. for $C_{30}H_{28}N_2O_6$: C 70.30, H 5.51, N 5.47%. Found: C 70.38, H 5.54, N 5.55%.

Crystallographic analysis. A single crystal of the dimensions $0.38 \times 0.14 \times 0.09$ mm of L^1 and the dimensions $0.54 \times 0.28 \times 0.13$ mm of L^2 was chosen for the X-ray diffraction study. Crystallographic measurements were performed at 120 K with a four-circle Oxford Diffraction Gemini CCD diffractometer with mirrors-collimated $CuK\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). The crystal structure was solved by charge flipping using the SUPERFLIP program [27] and refined with the Jana2006 program package [28] by the full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by ORTEP III [29]. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice, hydrogen atoms attached to carbon atoms were kept in ideal positions during the refinement. The methyl hydrogen atoms were allowed to rotate freely about the adjacent C—C bonds. The isotropic atomic displacement parameters of hydrogen atoms were set to $1.5U_{eq}(C)$ for methyl groups and to $1.2U_{eq}(C,N)$ for all other hydrogen atoms. Crystallographic data and details of the data collection and structure solution and refinements L^1 : $C_{30}H_{28}N_2O_6$, $M = 512.6$, monoclinic, space group $C2/c$, $a = 21.8589(14)$, $b = 4.7995(4)$, $c = 24.2047(18) \text{ \AA}$, $\beta = 104.496(6)^\circ$, $V = 2458.5(3) \text{ \AA}^3$, $Z = 4$, $\mu = 0.80 \text{ mm}^{-1}$, 11826 measured reflections, 2195 independent, 1645 observed ($I > 3\sigma(I)$), $R_{int} = 0.039$, $S = 1.71$, $R(F^2 > 3\sigma(F^2)) = 0.053$, $wR(F^2) = 0.145$, 175 parameters, $\Delta\rho_{max}/\Delta\rho_{min} = 0.42 / -0.21 \text{ e/\AA}^3$. L^2 : $C_{30}H_{28}N_2O_6$, $M = 512.6$, monoclinic, space group $C2/c$, $a = 14.4284(11)$, $b = 9.9660(6)$, $c = 17.8616(9) \text{ \AA}$, $\beta = 101.807(5)^\circ$, $V = 2514.0(3) \text{ \AA}^3$, $Z = 4$, $\mu = 0.78 \text{ mm}^{-1}$, 9844 measured reflections, 2243 independent, 1691 observed ($I > 3\sigma(I)$), $R_{int} = 0.040$, $S = 1.63$, $R(F^2 > 3\sigma(F^2)) = 0.050$, $wR(F^2) = 0.139$, 176 parameters, $\Delta\rho_{max}/\Delta\rho_{min} = 0.27 / -0.20 \text{ e/\AA}^3$.

Selected bond distances and angles are listed in Tables 1 and 2, respectively.

Results and discussion. The molecular structures of the titled compounds L^1 and L^2 with the atom numbering scheme are given in Figs. 1 and 2, respectively. Bond distances and angles (Tables 1 and 2) are in good agreement with the reports on similar compounds [20–25]. The bond distances N1—C7 (1.263(3) \AA) and N1—C1 (1.419(3) \AA) in L^1 and N1—C9 (1.267(3) \AA) and N1—C10 (1.429(3) \AA) in L^2 are consistent with the distances of the C—N double and single bonds [20–25]. The bond angles N1—C7—C8 (123.9(2) $^\circ$) and C7—N1—C1 (121.0(2) $^\circ$) in L^1 and N1—C9—C1

Table 1

Selected bond distances (Å) and angles (deg.) of L^1

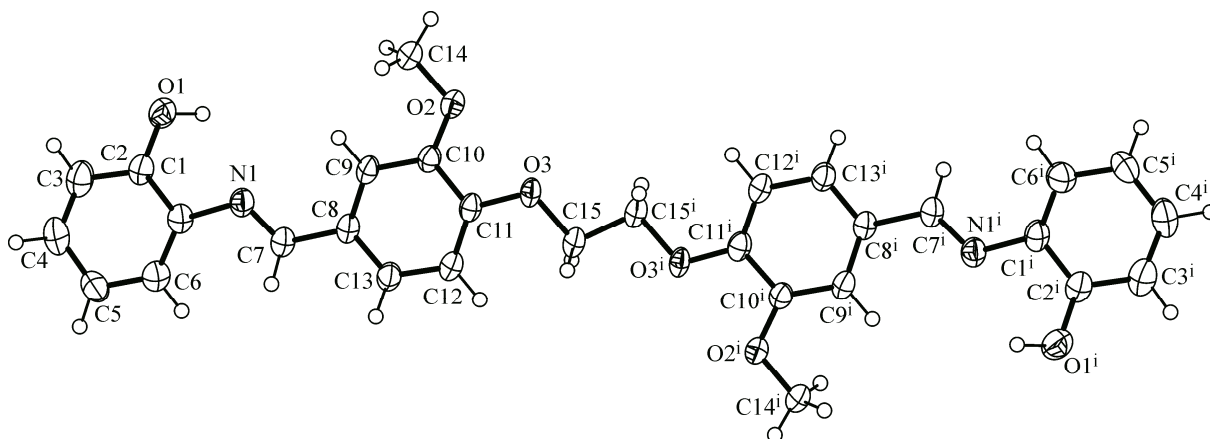
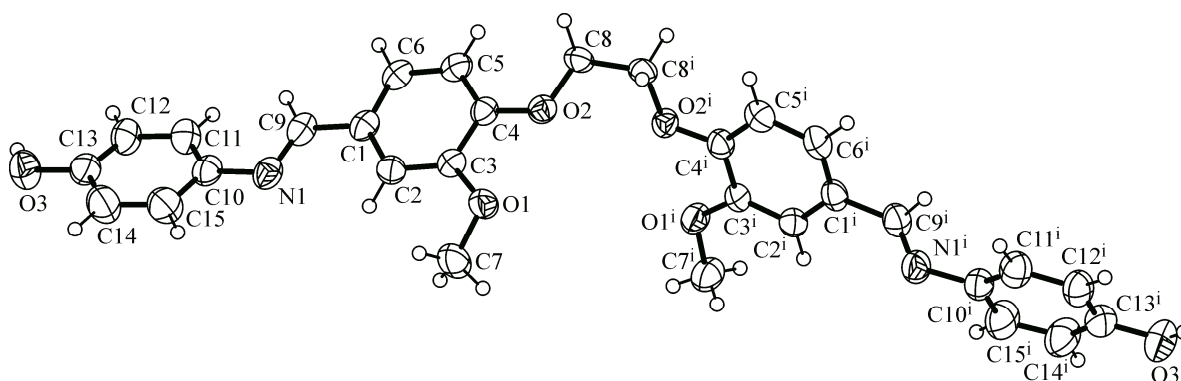
O1C2	1.358(3)	O3C15	1.443(2)	C10O2C14	115.78(17)	O2C10C9	125.33(18)
O2C10	1.360(3)	N1C1	1.419(3)	C11O3C15	116.13(17)	O2C10C11	114.88(18)
O2C14	1.436(3)	N1C7	1.263(3)	C1N1C7	121.0(2)	O3C11C10	115.56(19)
O3C11	1.360(2)	C15C15 ⁱ	1.501(3)	N1C1C2	114.8(2)	O3C11C12	124.83(18)
				N1C1C6	127.5(2)	O3C15C15 ⁱ	105.63(17)
				O1C2C1	120.2(2)	N1C7C8	123.9(2)
				O1C2C3	118.8(2)		

Symmetry codes: ⁱ -x, -y, 1-z.

Table 2

Selected bond distances (Å) and angles (deg.) of L^2

O3C13	1.365(3)	O2C8	1.440(2)	C3O1C7	117.65(19)	O1C3C4	114.43(18)
O1C3	1.377(3)	N1C9	1.267(3)	C4O2C8	117.27(16)	O1C3C2	125.08(18)
O1C7	1.425(3)	N1C10	1.429(3)	C10N1C9	118.4(2)	O2C4C3	114.79(18)
O2C4	1.353(3)	C8C8 ⁱ	1.489(3)	N1C10C11	126.0(2)	O2C4C5	125.45(17)
				N1C10C15	116.4(2)	O2C8C8 ⁱ	107.33(16)
				O3C13C12	123.0(2)	N1C9C1	123.5(2)
				O3C13C14	117.7(2)		

Symmetry codes: ⁱ -x, -y, 1-z.Fig. 1. ORTEP view of L^1 with 50 % probability displacement ellipsoids and atomic numberingFig. 2. ORTEP view of L^2 with 50 % probability displacement ellipsoids and atomic numbering

T a b l e 3 (123.5(2)°) and C10—N1—C9 (118.4(2)°) in **L**² are consistent with the *sp*² hybrid character of C7 and N1 atoms [20—25]. There is one intramolecular hydrogen bond of the O—H···N type in the compounds **L**¹ and **L**² (Table 3).

Compound	D—H···A	D—H	H···A	D···A	D—H···A
L ¹	O1H1oO1	0.88(2)	2.15(3)	2.905(3)	144(3)
L ²	O3H3oO1	0.91(2)	1.93(3)	2.817(3)	166(3)

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Center, CCDC Nos. 1021021 (**L**¹) and 1021022 (**L**²). 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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