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Short Note

N^1-Benzylidene-N^2-(2-((2-((2-(benzylideneamino)ethyl)amino)ethyl)amino)ethyl)ethane-1,2-diamine

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Abstract: A tetraethylene pentamine-diamine (**L^4**), the biggest compound in the family of dibenzylated diimine-polyamines (**L^1**–**L^4**) has been synthesized by classical Schiff-base reaction between benzaldehyde and the diamine tetraethylenepentamine, and the structure was confirmed by elemental analysis, ESI-MS spectrometry and by IR and ^{1}H-NMR spectroscopy.

Keywords: imine compounds; amine compounds; polyamines; dibenzylated

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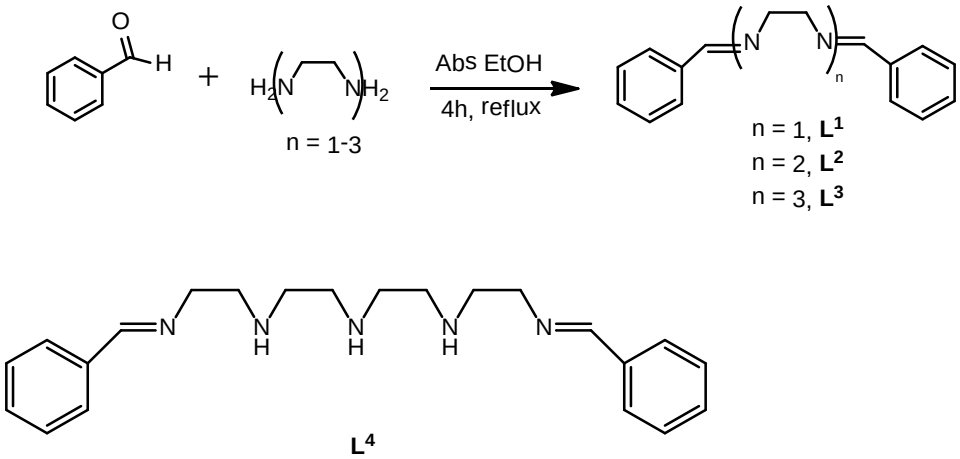
Improved understanding of the role of polyamines in metabolism [1,2], and the differences in polyamine biology between normal cells and tumor cells [3], have increased current interest in this type of compounds in the field of drug development [4,5]. The activity of polyamines is very much dependent on their charge and the charge density they display at physiological pH [6].

During the last ten years, some of us have been involved in the studies of many different water-soluble bis-chromophoric polyamines as fluorescent chemosensors [7–10]. However, more recently studies in new active MALDI-TOF-MS matrices reveals that the introduction of imine groups into the polyamine chain increases the energy absorbed in the UV region, and consequently, the potential application as a MALDI matrix increase [11,12].

Following the method previously reported by Bernardo *et al.* for polyamine systems [13], in this paper we describe the synthesis and characterization of the tetraethylene pentamine-diamine (**L**^{4}), derived from benzaldehyde and the diamine tetraethylenepentamine. The broader applicability of this method was demonstrated by the synthesis of a few related compounds (**L**^{1}–**L**^{3}) [14] (See scheme 1).

Scheme 1. Schematic representation of compounds **L**^{1}–**L**^{4}.



Experimental

A solution of benzaldehyde (0.129 g, 1.225 mmol) in absolute ethanol (20 mL) was added dropwise to a refluxing solution of tetraethylenepentamine (0.115 g, 0.612 mmol) in the same solvent (15 mL). The resulting solution was gently refluxed with magnetic stirring for 4 h. The colour changed from colourless to yellow. The solution was concentrated under vacuum to 1/3 of its volume. Diethyl ether was added to the solution and then cooled at 0 °C during 24 h. The yellow crystals formed were filtered off and dried under vacuum. At room temperature the crystals were not stable and a yellow oil was obtained.

L^{4}: *N*^{1}-Benzylidene-*N*^{2}-(2-((2-((2-(benzylideneamino)ethyl)amino)ethyl)amino)ethyl)ethane-1,2-diamine

Yield: 125 mg (56%).

ESI-MS: *m/z* (rel.int%): 366.26 (100) ([M+H]$^{+}$).

^{1}H-NMR ($CDCl_3$): δ = 8.3 (s, 2H, N=C–H); 7.5–7.7 (m, 4H, C-H_{ar}); 7.4–7.1 (m, 6H, C-H_{ar}); 3.8–3.2 (m, 4H, CH_2); 2.9–2.1 (m, 12H, CH_2) ppm.

IR (cm^{-1}): 1658 (C=N, Imine), 1589, 1492 (C=C, Ar).

Elemental analysis: Calcd for $C_{22}H_{31}N_5$: C, 72.29; H, 8.55; N, 19.16. Found: C, 72.26; H, 7.99; N, 19.65.

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14. The smaller parent compounds derived from 1,2-ethanediamine (**L**^{1}), diethylenetriamine (**L**^{2}), and triethylenetetramine (**L**^{3}) were obtained by a similar methodology, using 0.038, 0.063 and 0.089 g of diamine, respectively. Compound **L**^{1}: N^1,N^2-Dibenzylideneethane-1,2-diamine; Yield: 121 mg (84%); ESI-MS: *m/z* (rel. int%): 237.13 (100) ([M+H]$^+$); ^{1}H NMR ($CDCl_3$): δ = 8.1 (s, 2H, N=C–H); 7.8 (m, 4H, C-H_{ar}); 7.2 (m, 6H, C-H_{ar}); 3.8 (s, 4H, CH_2) ppm; IR (cm^{-1}): 1647 (C=N, Imine), 1599, 1498 (C=C, Ar); Elemental analysis: Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 80.87; H, 7.02; N,12.05. Compound **L**^{2}: N^1-Benzylidene-N^2-(2-(benzylideneamino)-ethyl)ethane-1,2-diamine; Yield: 103 mg (71%); ESI-MS: *m/z* (rel. int%): 279.17 (100) ([M+H]$^+$); ^{1}H-NMR ($CDCl_3$): δ = 8.2 (s, 2H, N=C–H); 7.8–7.6 (m, 4H, C-H_{ar}); 7.4–7.2 (m, 6H, C-H_{ar}); 3.8 (m, 4H, CH_2); 2.9 (m, 4H, CH_2) ppm; IR (cm^{-1}): 1649 (C=N, Imine), 1586, 1491 (C=C, Ar); Elemental analysis: Calcd for $C_{18}H_{21}N_3$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.16; H, 8.03; N, 15.34. Compound **L**^{3}: N^1,$N^{1'}$-(Ethane-1,2-diyl)bis(N^2-benzylideneethane-1,2-diamine); Yield: 132 mg (89%); ESI-MS: *m/z* (rel. int%): 323.22 (100) ([M+H]$^+$); ^{1}H-NMR ($CDCl_3$): δ = 8.1 (s, 2H, N=C–H); 7.7–7.5 (m, 4H, C-H_{ar}); 7.4–7.1 (m, 6H, C-H_{ar}); 3.7–3.4 (m, 2H, CH_2); 2.9–2.1 (m, 8H, CH_2) ppm; IR (cm^{-1}): 1656 (C=N, Imine), 1576, 1499 (C=C, Ar); Elemental analysis: Calcd for $C_{20}H_{26}N_4$: C, 74.50; H, 8.13; N, 17.38. Found: C, 74.78; H, 8.16; N, 17.49.