

Short Note

1,3-Bis{[(*E*)-(9-ethyl-9*H*-carbazol-3-yl)methylene]amino}propan-2-ol

Ismail Warad ^{1,*}, Nisreen Amer ¹, Huda Abedalrazeq ¹, Anas Al Ali ¹ , Nabil Al-Zaqri ², Hicham Elmsellem ³ and Abdelkader Zarrouk ³

¹ Department of Chemistry, An-Najah National University, P.O. Box 7, Nablus 0097, Palestine; nisreena135@hotmail.com (N.A.); huda123razeq@gmail.com (H.A.); anas.alali@najah.edu (A.A.A.)

² Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia; nalzaqri@ksu.edu.sa

³ LCAE-URAC18, Faculty of Sciences Oujda, University of Mohammed Premier, BP 4808, Oujda 60046, Morocco; h.elmsellem@yahoo.fr (H.E.); azarrouk@gmail.com (A.Z.)

* Correspondence: warad@najah.edu; Tel./Fax: +970-9234-5982

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Abstract: Condensation of 1,3-diaminopropan-2-ol with 9-ethyl-9*H*-carbazole-3-carbaldehyde in absolute ethanol under stirring condition resulted in the formation of 1,3-bis{[(*E*)-(9-ethyl-9*H*-carbazol-3-yl)methylidene]amino}propan-2-ol within 0.5 h in an excellent yield. The structure of the desired Schiff base was physically analyzed via CHN-elemental analysis, TOF-MS, UV-vis, FT-IR, and ¹H & ¹³C-NMR. Computational studies of the structure were performed at the DFT/B3LYP/6-311++G(d) level of theory. Molecular electrostatic potential (MEP), Mulliken charge, IR-B3LYP, and structure optimization were performed.

Keywords: DFT; Schiff base; complexing agent; condensation; optimization

1. Introduction

Schiff base (SB) (>C=N-) preparation, reported first by Hugo Schiff (1915–1834) [1], is considered a broad branch in the organic field of natural science. Compounds containing azomethine functional group compounds are usually prepared by condensation of primary amines (-NH₂) with aldehyde (R(=O)H) or ketone (R(=O)R') carbonyl compounds [2,3].

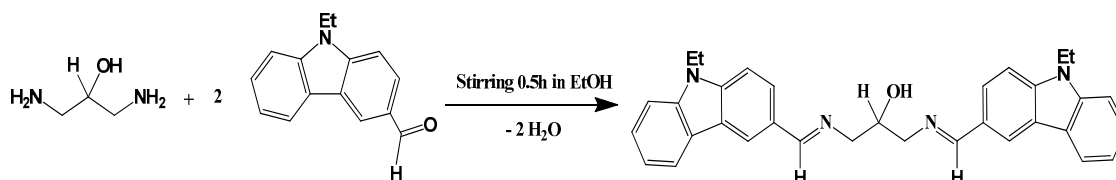
Considerable biological activity in antifungal, anti-apoptotic, anti-inflammatory, antiviral, and antibiotic agents has been documented for the above-mentioned compounds [4]. Beyond this, these compounds are of interest for their electroluminescent [5] and fluorescence properties [6] and hold promise as sensors [7], corrosion inhibitors [8], organic photovoltaic materials [9], and catalysts [10].

Due to the lone pair electrons on nitrogen, SBs are considered good metal complexing agents. Mono-, bi-, and poly-dentate complexing agents suitable for transition metal coordination via >C=N-, improving the complexes' physicochemical, pharmacological, and catalytic properties [11–15]. Regardless of the number of SB ligands and their complexes, there remains a need for new SBs and SB complexes with novel properties for new applications. In connection with previous work [2,16–18], 1,3-bis{[(*E*)-(9-ethyl-9*H*-carbazol-3-yl)methylidene]amino}propan-2-ol was prepared and analyzed, spectrally and DFT-computationally, in this study.

2. Results

1,3-Bis{[(*E*)-(9-ethyl-9*H*-carbazol-3-yl)methylene]amino}propan-2-ol was synthesized by condensing 2.2 equiv of 9-ethyl-9*H*-carbazole-3-carbaldehyde with 1 equiv 1,3-diaminopropan-2-ol in absolute ethanol under stirring conditions, as shown in Scheme 1. Within 0.5 h at room temperature (23 °C),

the desired SB product precipitated in high yield. One (diamine) to two (aldehyde) stoichiometry conditions ensured the formation of the desired SB without any heterocyclic side products [2]. The product was finally isolated as a white powder with m.p. = 201–205 °C. Further purification was achieved by recrystallization of the compound from dichloromethane. The compound was soluble in dichloromethane at room temperature, slightly soluble in ethanol, and insoluble in water hexane and ether, even at high temperature.



Scheme 1. Synthesis of 1,3-bis[[(*E*)-(9-ethyl-9*H*-carbazol-3-yl)methylene]amino]propan-2-ol.

Elemental analysis of 1,3-bis[[(*E*)-(9-ethyl-9*H*-carbazol-3-yl)methylene]amino]propan-2-ol was consistent with its proposed molecular formula. TOF-MS reflected an excellent agreement with the expected structure molecular weight, the experimental molecular ion [M^+] $m/z = 500.2$ (500.258, theoretical). Elemental analysis and TOF-MS of prepared SB were consistent with the proposed molecular formula (M^+) and (MH^+) molecular ion peak, as seen in Figure S1.

2.1. Electronic Transfer

The condensation reaction was monitored by UV/Vis in MeOH solvent. The completeness of the dehydration was supported by the change in the UV absorption behavior of the desired compounds relative to the starting materials. Four main absorption peaks belonging to the desired SB corresponded to ($n \rightarrow \pi^*$) and ($\pi \rightarrow \pi^*$) electron transfers at $\lambda_{\max} = 235, 275, 315,$ and 385 nm. No peak above 400 nm in the visible region was detected.

The experimental FT-IR of the 1,3-bis[[(*E*)-(9-ethyl-9*H*-carbazol-3-yl)methylene]amino]propan-2-ol indicated the presence of several functional groups on its structure (Figure S3a). DFT-IR B3LYP/6-311++G(d) calculation confirmed these as shown in Figure S3b. The main functional groups frequencies vibrations were listed as (V_{O-H} exp. = 3240, DFT = 3620 cm^{-1}), (V_{C-Hph} exp. = 3110, DFT = 3250 cm^{-1}), (V_{C-H} exp. = 2910, DFT = 2950 cm^{-1}), and ($V_{C=N}$ exp. = 1680, DFT = 1740 cm^{-1}) (Figure S3).

$^1\text{H-NMR}$ of the 1,3-bis[[(*E*)-(9-ethyl-9*H*-carbazol-3-yl)methylene]amino]propan-2-ol showed (1) five signals in the aliphatic region below 5 ppm reflecting 2CH₃, 2CH₂, 2CH₂-N, 1CH, and 1OH protons; (2) six signals of 14CH-aromatic protons in the $\delta_{\text{H}} = 7.2\text{--}8.0$ ppm range, and (3) one signal at 8.3 ppm for the two CH=N protons, as seen in Figure S4.

$^{13}\text{C-NMR}$ showed 7C with four-signals in the aliphatic region at 13–70 ppm, 24C with 12 signals in the aromatic region at 110–150 ppm, and 2C of aldimine at 165.0 ppm, as seen in Figure S5.

2.2. Optimization, Mulliken, and MPE Analysis

The B3LYP/6-311++G(d)-optimized bonds lengths and angles for 1,3-bis[[(*E*)-(3-bromobenzylidene)amino]propan-2-ol are shown in Table S6 and the optimized structure is illustrated in Figure S7a. The structure existed in the *E,E*-conformation with respect to the imine functional groups. The optimized conformation makes the compound suitable as an *N*-bidentate ligand for coordination of transition metal ions. The N=C bond lengths and C=N=C angles supported the sp^2 -hybridization character around both N atoms. Moreover, the aromatic rings on both sides were found to lie along the same axis but pointed in opposite directions, which expanded and flattened the molecule, reduced the internal molecular repulsion, and prevented phenyl stacking interactions within the molecule.

The Mulliken population charge analysis of the prepared SB was performed under the B3LYP/6-311++G(d) level of theory. Several positive and negative atomic charges were detected as shown in Figure S7b. All the hydrogen atom types reflected positive charges; the highest one was the polar hydrogen belonging to the hydroxide functional group. The majority of the atoms in the molecules, such as the 4N, 1O, and 26C atoms were assigned to have negative (nucleophilic) charges (C23 and C39 were the highest nucleophilic atoms). Only 4C reflected positive charges (C32, C27, C16, and C10 are electrophilic atoms). C3, C15, and C31 were found to be neutral with zero charge.

The MEP map analysis was consistent with the Mulliken result; several nucleophilic and electrophilic atoms on the molecule surface were assigned as in Figure S7c. Red indicates the electron-rich atoms, like O- and N-atoms with high nucleophilic behavior. Blue indicates the H atoms of the phenyl rings, together with the H atoms of the hydroxyl, which have electrophilic centers. The other atoms (green) were found to in between electrophilic and nucleophilic characters [2].

3. Materials and Methods

FT-IR analysis was carried out on a PerkinElmer-1000 FT-IR spectrometer (PerkinElmer Inc., Waltham, MA, USA). NMR was recorded on a DRX 250 Bruker-spectrometer (Bruker, Mainz, Germany). The UV-vis was analyzed on a double beam TU-1901 spectrophotometer (Purkinje General Instrument Co., Ltd., Beijing, China). MS was performed on a Finnigan 711A (8 kV) (PerkinElmer Inc., Waltham, MA, USA).

The compound was prepared following our recent modified procedure [2]. A solution of 1,3-diaminopropan-2-ol (1 mmol) and 9-ethyl-9H-carbazole-3-carbaldehyde (2.2 mmol) in EtOH (30 mL) was stirred for 0.5 h, at which time the desired product was deposited as a white precipitate. The reaction was completed without reflux. The precipitate was filtered and washed with water, ethers, and hexane.

Yield: 92% as a white powder, m.p. = 201–205 °C, was collected; molecular formula: C₃₃H₃₂N₄O; (Calcd. C, 79.17; H, 6.44 and N, 11.19. Found: C, 79.08; H, 6.31 and N, 11.03). [M⁺] *m/z* = 500.2 (500.8, theoretical). ¹H-NMR (250 MHz, DMSO-*d*₆): (ppm) 1.5 (m, 6H, CH₃CH₂), 3.5 (2m, 4H, 2NCH₂CH-), 3.7 (m, 4H, CH₃CH₂), 3.9 (m, 1H, -CH(OH)), 4.9 (br, 1H, CH(OH)) 7.2–8.0 (14H, Ph's), 8.3 (s, 2H, -HC=N-). ¹³C-NMR (62.5 MHz, DMSO-*d*₆): (ppm) 13.5 (2C, C-CH₃CH₂), 36.2 (2C, CH₃-CH₂), 59.3 (2C, =NCH₂CH(OH)CH₂N=), 69.0 (C, =NCH₂CH(OH)CH₂N=), 118.4, 116.6, 119.7, 119.8, 124.4, 128.2, 131.5, 131.6, 137.5, 139.8, 146.1, 149.6 (12 signals, 24C, Ph's), 164.8 (2C, -HC=N-). FT-IR main vibrations, *V*_{O-H} = 3240 cm⁻¹, *V*_{C-H_{ph}} = 3110 cm⁻¹, *V*_{C-H} = 2910 cm⁻¹, *V*_{C=N} = 1680 cm⁻¹, UV/Vis. Abs. in MeOH, λ_{max} = 235, 275, 315, and 385 nm.

4. Conclusions

A new Schiff base, 1,3-bis[[(*E*)-(9-ethyl-9H-carbazol-3-yl)methylidene]amino]propan-2-ol, was prepared in high yield via condensation of 1,3-diaminopropan-2-ol with 9-ethyl-9H-carbazole-3-carbaldehyde. All experimental measurements together with DFT/B3LYP analysis were in agreement with the expected molecular structure of the title compound.

Supplementary Materials: The following are available online www.mdpi.com/1422-8599/2018/1/M986/s1, Figure S1: TOF-MS spectrum of the desired SB, Figure S2: UV-spectra, (a) 1,3-diaminopropan-2-ol, (b) 9-ethyl-9H-carbazole-3-carb aldehyde and (c) 1,3-bis[[(*E*)-(9-ethyl-9H-carbazol-3-yl)methylene]amino]propan-2-ol in MeOH at RT, Figure S3: (a) Exp. FT-IR and (b) DFT-B3LYP/6-311++G(d) spectra, Figure S4: ¹H-NMR of the desired SB dissolved in DMSO-*d*₆, Figure S5: ¹³C-NMR of the desired product in DMSO-*d*₆, Table S6: Bond length and bond angle of the compound, Figure S7: (a) DFT-optimization, (b) Mulliken charge and (b) MEP map analysis.

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Author Contributions: N.A., H.A., and A.A.A. performed the experiments; N.A.-Z. measured and analyzed the NMR; H.E. measured and analyzed the MS; A.Z. and I.W. wrote the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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