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## NH-form of a threonine-based Schiff base in the solid state

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### Abstract:

Stable NH-form of the threonine-based Schiff base **4**, (2*S*,3*R*)-3-((*tert*-butyldimethylsilyl)oxy)-2-(((*E*)-(2-hydroxynaphthalen-1-yl)methylene)amino)butanamide, was synthesized and characterized in the crystalline state by means of IR spectroscopy and X-ray crystallographic analysis. This is the first X-ray determination of an amino acid-based Schiff base that was locked in the NH-form. Comparison of the characteristic bond lengths based on the X-ray structure of **4** with previously reported NH-forms of other Schiff bases revealed that the structure of **4** was a hybrid of two canonical structures, namely, zwitterion and quinoid, contributing to the resonance. It was also found that **4** exist in the OH-form in solution and its phenolic proton is well-constrained via intramolecular hydrogen bonding with the imine functionality.

### Keywords:

Schiff base, imine-phenol/keto-amine, tautomerism, zwitterion, quinoid

### Introduction:

Proton transfer during intramolecular hydrogen bonding, i.e. tautomerism, is of considerable interest to both chemists and biochemists. This chemical equilibrium plays an important roles in several biomolecular phenomenon, including the paramount stabilization of base pairs in the DNA

double helix [1–3]. Its relevance in the field of material science has also been highlighted recently in relation to thermochromic and photochromic properties of materials [4–7]. Therefore, although discovered a long time ago, study of proton tautomerization is a major scientific issue [8–11]. In this context, the NH-form in the imine-phenol/keto-amine tautomerization of salicylideneaniline shown in Figure 1 has been widely studied [12–18] since Ogawa et al. first provided X-ray crystallographic evidence of its existence [12,17]. The OH-form of salicylideneaniline is generally more stable than the NH-form and there are numerous studies on the properties involving the chromism of the OH-form of such molecules [19–22]. Besides, the NH form of the different compounds shown in Figure 2 was investigated by Ogawa et al., [12,17] Chong et al., [13] and Karabiyik et al. using single crystal X-ray diffraction (SC-XRD). In their study, Ogawa et al. have highlighted that compound **1** predominantly exists as a zwitterion (Figure 1) at 15 K but an unresolved disorder between the NH- and OH-forms appeared at temperatures higher than 90 K, although some doubt remains about the actual form, i.e., quinoid or zwitterion, for the NH tautomer [16]. Chong et al. reported that **2** exists as the quinoid-type of the NH-form in both solid and solution states at room temperature by using SC-XRD and NMR spectroscopy [13]. Karabiyik et al. concluded, based on characteristic bond lengths, that the molecular structure of compound **3** was actually an intermediate between the OH-form and quinoid-type NH-form [16].

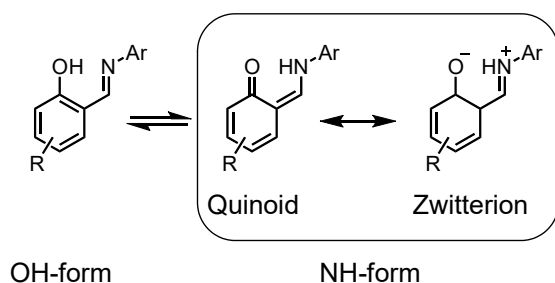


Fig 1. Tautomerization of salicylideneanilines showing the two canonical structures that contribute to the resonance structure of the NH form.

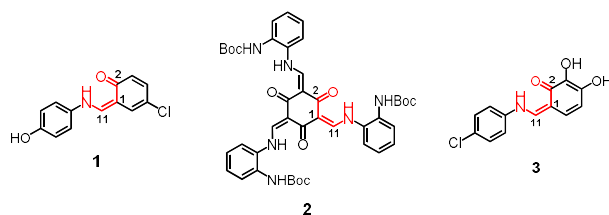


Fig 2. Chemical structures of salicylidenanilines reported as NH-form. Atomic numbering is the same as that used in Fig 4.

In this study, the threonine-based Schiff base **4** (Scheme 1) was synthesized and its solid form was characterized by IR spectroscopy at room temperature and by SC-XRD at 100 K. Both techniques indicated that **4** is as the NH-form in the solid state whatever the temperature. Closer inspection of the experimental data revealed that the compound is a hybrid of the two canonical structures, quinoid and zwitterion, contributing to the resonance structure. Further analyses by NMR and UV spectroscopy revealed that imine-phenol/keto-amine equilibrium occurs in chloroform, with the predominance of the OH form.

### Experimental section:

Synthetic procedure and preparation of a single crystal of **4**:

To the solution of L-threonine derivative, L-NH<sub>2</sub>-Thr(OTBS)-CONH<sub>2</sub>, in methanol, 2-hydroxy-1-naphthaldehyde was added and the mixture was refluxed for 3 h, followed by hot filtration. The solution was cooled to -20 °C, and the resulting precipitates were filtered and washed with ether. Yellow needle crystals were obtained in 95% yield. Single crystals were prepared by the slow evaporation of the solution of **4** in ethyl acetate and heptane (1:1, v/v) solution at 40 °C. M.P. 178.9 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm) 0.08 (s, 3H), 0.11 (s, 3H), 0.92 (s, 9H), 1.24 (d, 3H, *J* = 9.0 Hz), 1.69 (br, 2H), 3.89 (s, 1H), 4.53 (m, 1H), 5.68 (br, 1H), 6.32 (br, 1H), 7.08 (d, 1H, *J* = 9.3 Hz), 7.32 (t, 1H, *J* = 7.4 Hz), 7.50 (t, 1H, *J* = 7.2 Hz), 7.70 (d, 1H, *J* = 7.8 Hz), 7.79

(d, 1H,  $J = 9.1$  Hz), 7.98 (d, 1H,  $J = 8.5$  Hz), 8.96 (d, 1H,  $J = 3.3$  Hz), 14.40 (br, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.2, 169.7, 161.6, 136.5, 133.0, 129.3, 128.1, 127.1, 123.5, 122.1, 118.7, 108.2, 76.2, 69.2, 25.7, 20.6, 17.9, -4.5, -5.2; FTIR (ATR)  $\nu_{\text{max}}$ : 3362, 3179, 2955, 2931, 2856, 1665, 1624, 1520, 1471, 1347, 1313, 1253, 1131, 1094, 989, 832, 812, 777, 745, 671, 639, 444, 414  $\text{cm}^{-1}$ ; UV-Vis,  $l_{\text{abs}}$  (nm) [ $\log \epsilon_{\text{abs}}$ ]: 420 [4.00], 402 [3.98], 304 [3.98], 252 [4.24], 231 [4.61]. HRMS (ESI): Calcd for  $\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_3\text{Si}$   $[\text{M}+\text{H}]^+$  387.2104; found 387.2108. Anal. Calcd for  $\text{C}_{21}\text{H}_{30}\text{N}_2\text{O}_3\text{Si}$ : C, 65.25; H, 7.82; N, 7.25. Found C, 65.28; H, 8.13; N, 7.11%.

#### X-ray crystallographic analysis

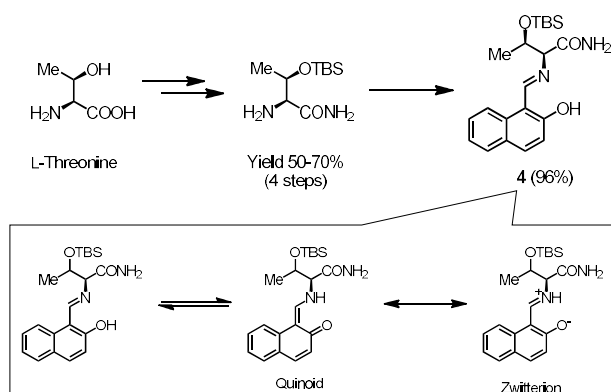
X-ray diffraction data were collected using a Rigaku Saturn724+ CCD area detector diffractometer mounted on a  $1/4\lambda$  goniometer [graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å);  $\omega$  scans] assembled together with a Rigaku low-temperature equipment. All the structures were solved by direct methods using SIR97 [23] and refined on  $F^2$  with all data using SHELXL-2014/7 [23]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically or using the riding model. All calculations were performed using Yadokari XG2009 [24]. Software program Mercury[25] was used for analysis and visualization. Crystallographic data for the structure reported in the paper have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 1868653. Crystallographic data for **4**: Monoclinic, space group  $P2_1$ ,  $a=11.734(3)$  Å,  $b=6.498(2)$  Å,  $c=14.357(4)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 90.586^\circ(3)$ ,  $\gamma = 90^\circ$ ,  $V= 1094.7$  Å<sup>3</sup>,  $Z=2$ ; in the final least-squares refinement cycles on  $F^2$ , the model converged at Final  $R_1$  values ( $I > 2\sigma(I)$ )=0.0282, Final  $wR(F_2)$  values ( $I > 2\sigma(I)$ )=0.0636, and GOF=0.948 for 4947 reflections.

#### *Ab initio* quantum calculations

Structural optimization of the NH- and OH-forms of **4** was performed at the B3LYP/6-31G(d) level of theory using the Firefly (Version 8) QC package [26,27] in the Winmostar (Version 8) program [28]. Theoretical  $^{13}\text{C}$ -NMR chemical shifts of the NH- and OH- forms of **4** were calculated at the B3LYP/6-31+G(d,p) level of theory with the GIAO method using the ORCA program system (Version 4.0) [29].

### Results:

The precursor of compound **4**, a L-threonine derivative, was synthesized by using a four steps procedure described in the literature [30] using L-threonine as starting materials. A similar moderate yield was obtained. Subsequent condensation of the L-threonine derivative and 2-hydroxy-1-naphthaldehyde gave compound **4** with a satisfactory yield (Scheme 1).



Scheme 1. Synthesis of threonine-based Schiff base **4**, and its resonance structures.

The molecular structure of **4** is shown in Figure 3 with atom numbering, and detail crystallographic data is in supporting information. The positions of all hydrogen atoms, except for the methyl group, were determined from usual refinement of the initial positions based on the electron density peaks. This SC-XRD analysis clearly revealed that compound **4** exists as the NH-form at 100 K (see Figure S8). In contrast to compound **1** for which crystalline disorder between the NH and OH forms are observed above 90 K, tautomerization equilibrium of **4** is completely

shifted to the NH-form even at 100 K, indicating that the NH configuration is more stable for **4** than for **1**.

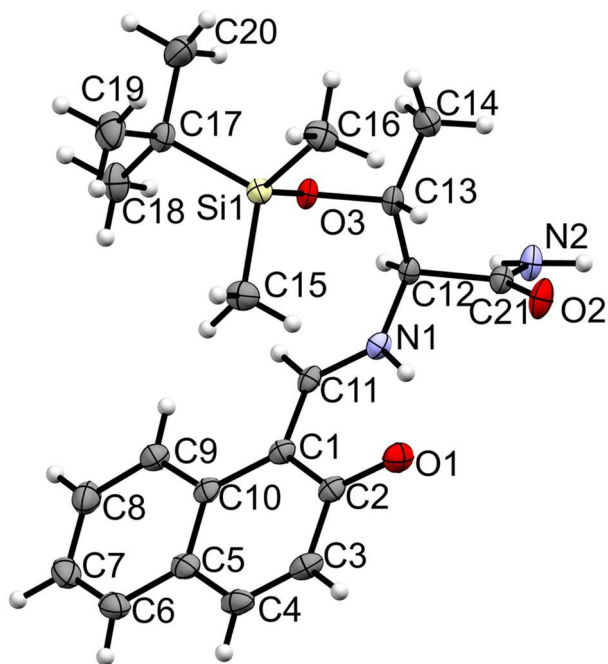


Fig 3. Molecular structure of compound **4** in the crystal structure (thermal ellipsoids are shown at 50% electron density).

This result can be explained by the different basicity of the nitrogen atom arising from the substituent. In general, the alkyl substituents exert a stronger inductive effect than aromatic substituents, which can stabilize the resulting electron-deficient NH-form. This result implies that using a stronger base to synthesize the Schiff base is very important for stabilization of the NH-form. In addition, *ab initio* DFT calculations revealed that the NH form of **4** is more stable than the OH form by  $\Delta H_f = -45.4$  kJ/mol. This result indicated that the stability of the NH form is due to the thermodynamic reasons rather than the additional intermolecular interactions in the crystal. Figure 4 summarizes the characteristic bond lengths of the reported NH-form and the expected

bond lengths of the quinoid and zwitterion structures have been estimated from statistical data [31]. These observations suggested that the hybrid of the aforementioned two canonical structures existed in the crystals. First, the N1–C11 bond was significantly shorter than the standard C(sp<sup>2</sup>)–N bond of the enamine (1.355 Å) and closer to that of an C(sp<sup>2</sup>)=N bond connected to an aromatic ring (1.279 Å) [31]. Second, the O1–C2 bond was considerably longer than the standard C=O bond in a conjugated enone (1.222 Å) and shorter than the C–O bond in phenols (1.362 Å) [31]. These facts indicated that the C–N and C–O bonds have intermediate behaviors between single- and double-type bonds. In the same manner, the C11–C1 and C1–C2 bonds showed intermediate character between single and double bonds. Indeed, the C1–C2, C2–C3, and C1–C10 bonds in the naphthyl ring were found to be significantly longer than the standard C–C bonds in a naphthyl ring (1.36, 1.42 Å), indicating that these bonds exhibit stronger single bond behavior than that of a naphthyl ring. In terms of cross-conjugation, this observation is also consistent with the valence bond model of the quinoidal and zwitterionic forms. From these observations, it is evident that compound **4** would exhibit properties that are between those of a zwitterion and a quinoid, e.g. delocalized ionic property as in a non-classical ion.

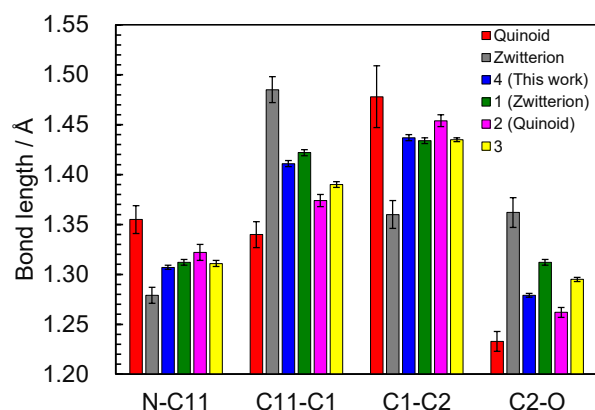


Fig 4. Characteristic bond lengths of the NH-forms in the crystals and expected bond lengths of quinoid and zwitterion structures [31]; red: quinoid, gray: zwitterion, blue: **4**, green: **1**, magenta:



2, yellow: 3. Error bar means mean estimated standard deviation.

ATR-IR spectrum of **4** in the solid phase was recorded at room temperature (Figure 5). In the higher wavenumber region, the symmetric and antisymmetric stretching of primary amide (-CONH<sub>2</sub>) were observed at 3362 and 3179 cm<sup>-1</sup>, respectively, and the absorption bands from 2856 cm<sup>-1</sup> to 2955 cm<sup>-1</sup> could be assigned to C-H stretching. The absorption bands between 1700–1550 cm<sup>-1</sup> could be attributed to the stretching vibrations of C=N and C=O groups. The carbonyl group of the primary amide showed an intense and sharp band at 1665 cm<sup>-1</sup>. The intense absorption band at ~1624 cm<sup>-1</sup> clearly included two shoulder peaks (zoom inlet in Figure 5). According to Salman et al., the carbonyl group of the keto-amine tautomer shows intense absorption bands at 1624–1633 cm<sup>-1</sup> [32]. In accordance with published data showing that stretching of the C=N bond occurs in the 1614–1623 cm<sup>-1</sup> region, the absorption at 1610 cm<sup>-1</sup> was attributed to the C=N group [5,18,32,33]. In addition, the occurrence of a zwitterion form decreases the wavenumber of this absorption since protonation of the nitrogen would increase the effective mass. Thus, the peak observed at ca. 1600 cm<sup>-1</sup> was attributed to stretching of C=NH<sup>+</sup> [32].

One should note that if **4** existed as the OH-form in the crystalline state, the characteristic intense O-H stretching at ~3100 cm<sup>-1</sup> would be observed which does not appear to be the case [15]. Thus, ATR-IR spectroscopy confirms that **4** exists as the NH-form in the solid state at room temperature. In addition, although the dominant canonical structure could not be quantitatively measured, these results imply that the NH form comprises the resonance hybrid of two structures, i.e. a mixture of quinoid and zwitterionic forms in the crystalline state at room temperature.

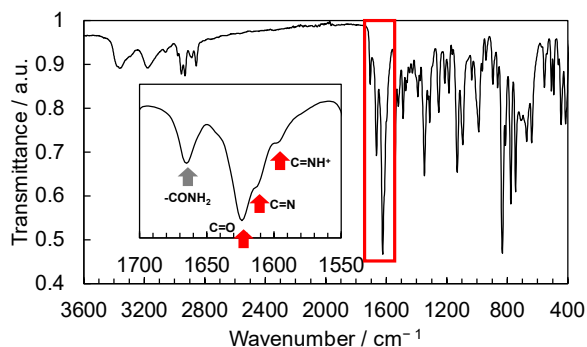


Fig 5. ATR-IR spectrum of **4** at room temperature.

$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectroscopy experiments and *ab initio* quantum calculations in  $^{13}\text{C}$ -NMR clarified that in chloroform ( $\text{CDCl}_3$ ,  $\text{CHCl}_3$ ), the phenol-imine/keto-amine equilibrium of compound **4** is shifted to the OH side and that the hydroxy proton is constrained on the oxygen. In the  $^1\text{H}$ -NMR spectrum of **4** in  $\text{CDCl}_3$  (Figure 6), the singlet peaks at 14.40 ppm and 8.96 ppm were assigned to the hydroxy and azomethine protons, respectively. Usually, phenolic protons are exchangeable with residual water in a deuterated solvent, so that a broad peak is observed in the spectrum. In contrast, the NMR spectrum of **4** showed a very sharp peak at 14.4 ppm corresponding to the phenolic proton, indicating that this proton is non-exchangeable and is constrained by the phenolic group. Figure 7 shows the correlations between the calculated chemical shifts of the NH- and OH- forms of **4** as well as the observed chemical shift in  $\text{CDCl}_3$ . There was only a slight difference between the calculated chemical shift of the OH-form and the observed shift, i.e., the two values matched well in general. In particular, the calculated chemical shifts of the OH-form around the aromatic region (100–150 ppm) were almost identical to the observed chemical shifts. Hence, it could be concluded that compound **4** mainly exists in the OH-form.

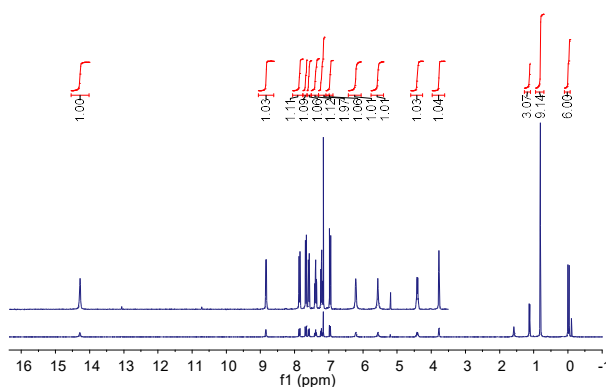


Fig 6.  $^1\text{H}$ -NMR spectra of **4** in  $\text{CDCl}_3$ .

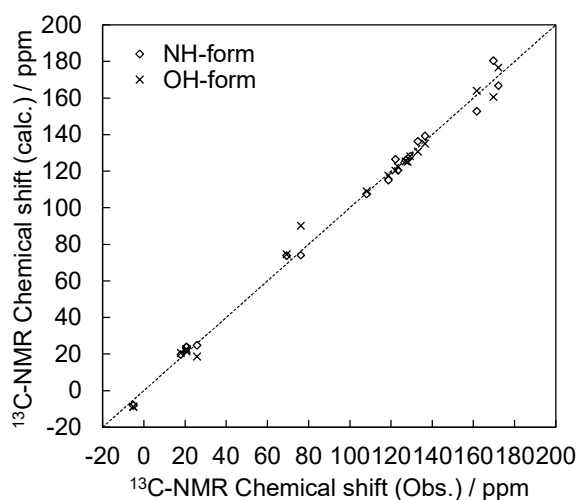


Fig 7. Calculated and observed  $^{13}\text{C}$ -NMR chemical shifts of NH- and OH- form of **4** in  $\text{CDCl}_3$ .

When the calculated and observed chemical shifts are identical, the points are on the dashed line.

The results of UV-Vis spectroscopic analysis also support this conclusion. According to the report by Fabian *et al.*, the OH- and NH-forms show absorbance at 350–400 nm and 420–500 nm, respectively, and the tautomerization equilibrium is shifted toward the OH-form in less polar solvents [34]. In  $\text{CHCl}_3$  and tetrachloromethane ( $\text{CCl}_4$ ), compound **4** showed strong absorbance at around 360 nm, which could be assigned to the OH-form. In contrast, this absorbance decreased in polar solvents, MeOH and DMSO. Thus, it could be considered that the equilibrium between the OH- and NH-forms of **4** is shifted toward the OH-form in  $\text{CHCl}_3$ .

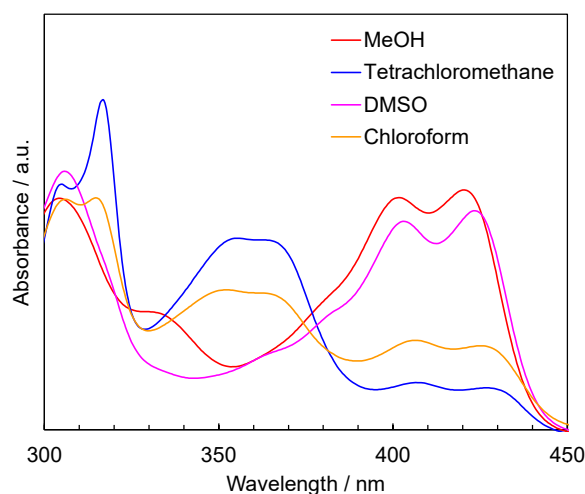


Fig 8. UV-Vis spectra of **4** in MeOH, tetrachloromethane, DMSO, and chloroform.

### Conclusion:

In conclusion, the threonine-based Schiff base **4** was prepared and SC-XRD and ATR-IR revealed that its molecular structure in the crystal is locked in the NH-form up to room temperature. Disorder between the quinoid and zwitterionic forms have been also evidenced. The OH-form mainly exists in the chloroform solution, and the equilibrium is shifted toward the NH-form in polar solvents. Therefore, this paper reports for the first case a stable NH-form among non-aromatic amine based-compounds that exhibit phenol-imine/keto-amine tautomerization at room temperature. In this context, the present study can provide insights into the NH- molecular structure for further understanding of the phenol-imine/keto-amine tautomerization.

### Supplementary material

NMR spectra of **4**, crystallographic data of **4**, and UV-Vis spectrum (PDF).

X-ray crystallographic data for **4** (cif).

Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road,

Cambridge CB2 1EW, U.K. (Email:deposit@ccdc.cam.ac.uk). CCDC 1868653.

### **Conflicts of interest**

There are no conflicts to declare.

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