Intramolecular Proton Transfer Inducing a Biszwitterion Structure in a N_4 Schiff Base

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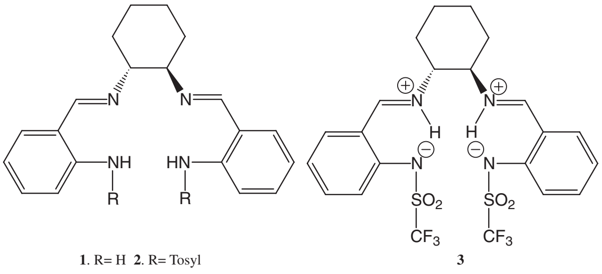
X-ray and NMR evidences of a sulfonated and tetradentate N_4 Schiff base pointed out unusual iminium groups. This produces amide groups and the protons transfer leads to an overall biszwitterion structure.

Tetradentate Schiff bases are among the most used ligands in asymmetric catalysis, such as Salen ligands which have the potential catalytic activities and are able to complex a variety of metals, and then catalyse several reactions in fine organic synthesis.[1–4] We have recently synthesized new chiral tetradentate N_4 Schiff bases containing sulfonamide functionalities.[5] The electron withdrawing sulfonyl group modifies the properties of the protons bound to the nitrogen atoms (Figure 1) and their chemical shifts vary from 6.3 ppm in 1 (R = H) to 13.2 ppm in **2**[6] (R = tosyl) and 14.8 ppm in **3** (R = triflate). We carried out the X-ray structure studies of these compounds and observed that an unexpected N–H bond occured with the imine N atoms in the triflic derivative **3**. The proton transfers result in the formation of a biszwitterionic structure and unexpected N^+–H···N^- interactions are directly observed. Very recently ionic hydrogen bonding was observed in Schiff bases involving N–H···O interactions.[7]



1. R= H **2**. R= Tosyl

3

Figure 1. Tetradentate N_4 Schiff bases **1**–**3**.

Tetradentate Schiff base **3** was prepared from **1** and Tf_2O at 195 K under a water free atmosphere.[5] Crystallization occurs at room temperature from either a 1/1 mixture of CH_2Cl_2/*n*-heptane or in pure MeOH, leading to crystals of Form A or Form B, respectively.[8] The asymmetric unit in Form A contains a single molecule while there are two independent molecules in the crystal of the Form B. Thus, the X-ray crystal analyses allow to describe independently three molecules of compound **3** and an ORTEP view of the Form A is given in Figure 2 (ORTEP view of Form B is available in the supporting information file). Selected distances and torsion angles are given in Table 1.

In any event, in the three X-ray structures the hydrogen atom positions H7 and H23 have been clearly evidenced by means of a Fourier map and their *x*, *y*, *z* parameters have been correctly refined.[8] The N7–H7 and N23–H23 bond distances are comprised between 0.72(4) and 1.07(7) Å, while N15···H7 and N31···H23 distances are much longer: from 1.78(7) to 2.14(8) Å.

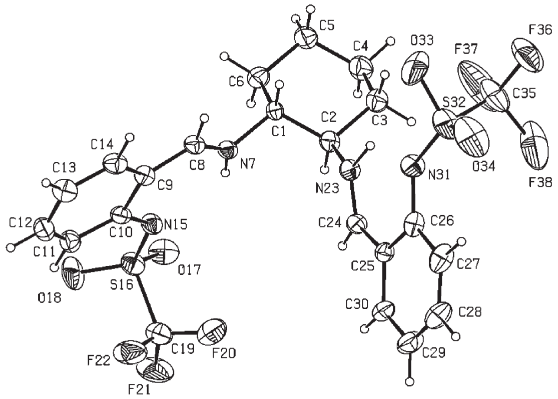


Figure 2. ORTEP view of crystal Form A.

Table 1. Selected distances (Å) and torsion angles (°) of **3**.

	Form A	Form B 1st molecule	Form B 2nd molecule
N7···H7	0.77(8)	0.97(5)	0.76(5)
N23···H23	1.07(7)	0.72(4)	0.91(5)
N15···H7	2.14(8)	1.79(5)	1.93(5)
N31···H23	1.78(7)	1.94(5)	1.82(5)
N7···N23	3.008(8)	2.888(5)	2.861(5)
N7···N15	2.657(8)	2.587(5)	2.589(5)
N23···N31	2.614(8)	2.579(5)	2.577(5)
N31···N15	7.324(8)	5.205(5)	4.694(5)
N7–C1–C2–N23	−64.9(7)	−51.2(4)	−57.9(4)
C2–C1–N7–C8	128.0(7)	−57.4(5)	−166.9(4)
C1–C2–N23–C24	118.5(7)	−97.8(5)	148.2(4)

We can thus assume that when the NH_2 group of **1** is replaced by the NH(Tf) group in **3**, the protons are transferred from N15 and N31 to N7 and N23, respectively. Concerning with the N···N distances, data of Table 1 shows a conformation change by means of the rotation of the trifluoromethylsulfonamidobenzylidene moieties around the C1–N7 and C2–N23 bonds. The imine N atoms are separated by about 2.9 Å in the three molecules but the distance between the two amine N atoms varies from 4.694(5) to 7.324(8) Å. This flexibility may facilitate the further coordination to metal atoms of very different sizes.

The NMR study of **3** was carried out in a $CDCl_3$ solution.[9] In the ^{1}H NMR spectrum we detect a resonance at 14.8 ppm with a broad line width at room temperature (50 Hz) but sharper at 213 K (21 Hz), revealing an exchange process affecting the NH protons. A Gaussian apodization of FID (LB $= -10$ Hz, GB $=$ 0.1) at 213 K shows that this peak has a doublet of doublet structure. The origin of this fine structure is given by cosy-1-D experiments (Figure 3): if we consider only one moiety of the molecule, H7 is coupled with H8 ($^3J = 8.8$ Hz), and H1 ($^3J =$ 5.5 Hz). At 213 K the protons are in a slow exchange mode and are therefore linked to the nitrogen atoms of the imine groups.

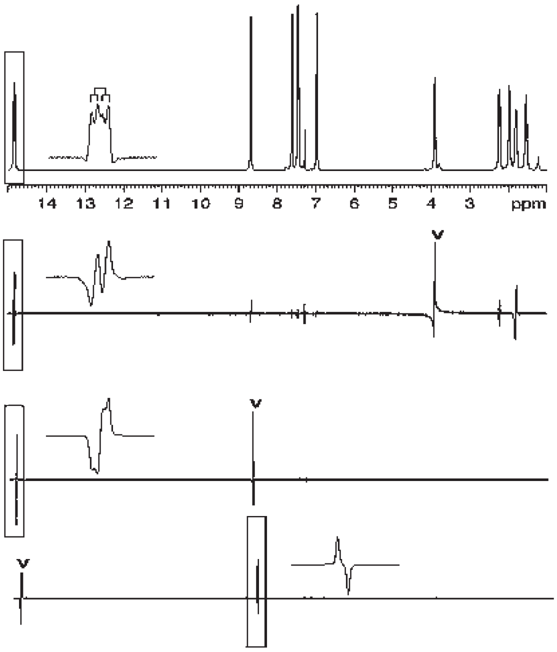


Figure 3. Cosy-1-D for compound **3** at 213 K. δ in ppm: 14.8 (H7, H23); 8.7 (H8, H24); 7.6 (H14, H30); 7.47 (H11, H27); 7.4 (H13, H29); 7 (H12, H28); 3.9 (H1, H2); 2.2 and 1.8 (H3, H6); 2 and 1.5 (H4, H5). v: Arrows indicate the frequency of selective excitation. The expansion of the coupled proton is drawn beside.

The nitrogen resonances are easily detected by 2-D HSQC experiments for temperatures lower than 283 K, and their attribution confirmed by ^{1}H-^{15}N HMBC (^{1}H-^{15}N, 2-D HSQC and ^{1}H-^{13}C HMBC spectra at 213 K are available in the supporting information file).[10] Same experiments were carried out on compound **2** and the results are summarized in Table 2. The $^1J_{NH}$ coupling constants evolve with temperature and N7 and N15 are coupled with the same proton. The greater $^1J_{NH}$ value observed for the N7–H7 interaction in compound **3** confirms that at 213 K, the proton is closer to the imine than to the sulfonamide group.

Table 2. ^{15}N NMR data for compounds **2** and **3**

Compound	N7		N15	
T/K	δppm	$^1J_{NH}$ (Hz)	δppm	$^1J_{NH}$ (Hz)
3 (283 K)	258	−22	124	−28
3 (213 K)	227	−51	130	−31
2 (213 K)	322	≈4	119	−83

In comparison at same temperature, for compound **2**, the greater $^1J_{NH}$ value corresponds to the stronger interaction due to the H–N15 bond. We also observe that for compound **3** a temperature decrease induces an opposite side displacement of the chemical shifts of N7 and N15 (the upfield shift of N7 and the downfield shift of N15) reflecting the evolution of the N7–H···N15 interactions.

In summary, the NMR study of product **3** at 213 K shows that the central hydrogen atoms tend to be located on the imine N atoms rather than on to the sulfonamide N atoms and thus confirm the unexpected N–H bond detected in the X-ray structure studies. Triflic derivative **3** is to our knowledge the first reported tetradentate N_4 Schiff base containing H on imine groups and is therefore a biszwitterion. We are now focussing on the preparation of various metallic complexes with **3** and observe that its particular structure facilitates the reactions. Introducing sulfonamido groups can induce significant changes in the complexation properties of a ligand. This behaviour may thus be considered to other sulfonamido ligand derivatives.

References and Notes

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8 Compound **3**, formula: $C_{22}H_{22}F_6N_4O_4S_2$ and M $=$ 584.56, shows polymorphism according to the crystallization solvent: **Form A.** Crystal from CH_2Cl_2/*n*-heptane (1/1); size (mm) : $0.25 \times 0.20 \times 0.15$; Orthorhombic; Space group : $P\ 2_1\ 2_1\ 2_1$; $a = 8.2240(2)$ Å; $b = 8.6820(2)$ Å; $c = 35.881(1)$ Å; $V =$ 2561.9(1) Å^3; $\rho = 1.516\,\mathrm{g\,cm^{-3}}$; $2\theta_{max} = 48.2°$; Mo Kα; 295 K; 8509 measured reflections; 3602 independent reflections included in the refinement; µMo Kα $= 0.289\,\mathrm{mm^{-1}}$; $T_{min} = 0.931$; $T_{max} = 0.958$; SHELXTL; 349 parameters; x, y, z of H7 and H23 (N–H) refined, all others introduced at their ideal positions; $R = 0.075$, $wR = 0.194$; refinement of F^2 against all reflections; $\Delta\rho_{max} = 0.95$, $\Delta\rho_{min} = -0.35\,\mathrm{e\,Å^{-3}}$, CCDC number: 194698. **Form B.** Crystal from MeOH, available in supporting information file. CCDC number: 225854

9 The NMR analysis are based on 1-D and 2-D experiments on a BRUKER DRX500 spectrometer, with a triple tuned probe ^{1}H–^{13}C–^{15}N. The 1-D-cosy experiments were acquired with the standard BRUKER selcogp micro program.

10 For ^{1}H-^{15}N HMBC and HSQC experiments, external NH_3 is used as reference (nitromethane resonating at 381.56 ppm). The gradient HMBC experiment used the standard sequence inv4gplrnd, and the measurement of N–H coupling constants, a homemade modified invietgs sequence, where the last refocusing echo and the ^{15}N decoupling is suppressed to detect directly the antiphase magnetisation.

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