

Imine-tetrahydroquinazoline tautomerism in a tosilated Schiff base

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Abstract

Condensation of the selectively tosilated *N*-(2-aminobenzyl)-4-methylbenzenesulfonamide with 2-hydroxybenzaldehyde gives rise to (*E*)-*N*-(2-(2-hydroxybenzylideneamino)benzyl)-4-methylbenzenesulfonamide in the solid state, as the crystal structure determined shows, and which in solution shows equilibrium between the acyclic imine and 2-(3-tosyl-1,2,3,4-tetrahydroquinazolin-2-yl)phenol

Introduction

Since a Schiff base ligand derived from *N*-(2-aminobenzyl)-4-methylbenzenesulfonamide [1], gave rise to novel μ_2 -*N*-sulfonamide bridges that appear to mediate a ferromagnetic interaction in a dimeric copper(II) complex [2], we decide to prepare new ligands to obtain new metal complexes. But prior to synthesising metal complexes, a suitable characterisation of the ligands designed is very useful. Thus, here we present a new Schiff base derived from the monotosylated diamine mentioned.

Results and discussion

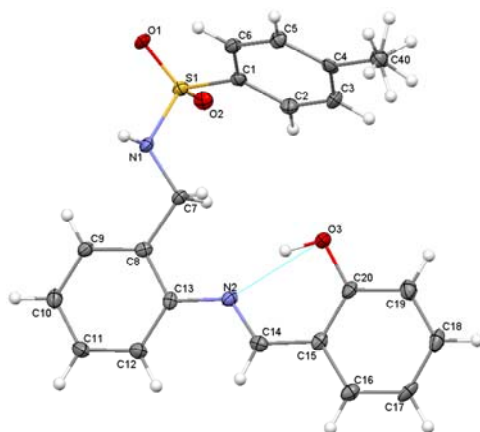
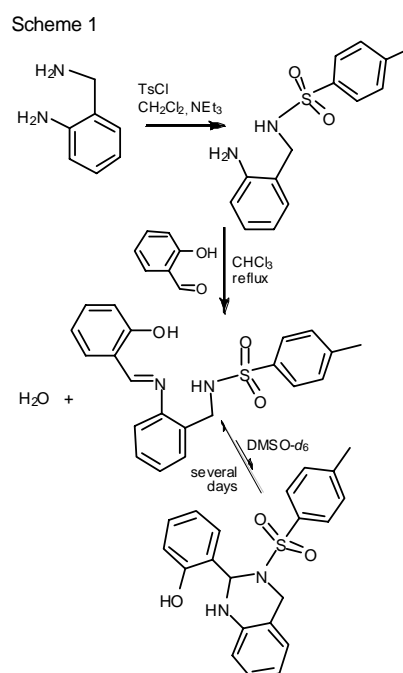
The first step of the synthetic procedure (Scheme 1) was the selective monotosylation of the diamine [1]. The second phase involves a simple Schiff condensation with salicylaldehyde that occurs with good yield (90%).

The powdery solid isolated only seems to contain the linear acyclic Schiff base, according to its characterisation data (EA, MS, FT-IR and NMR), and after recrystallisation, its crystal structure could be determined.

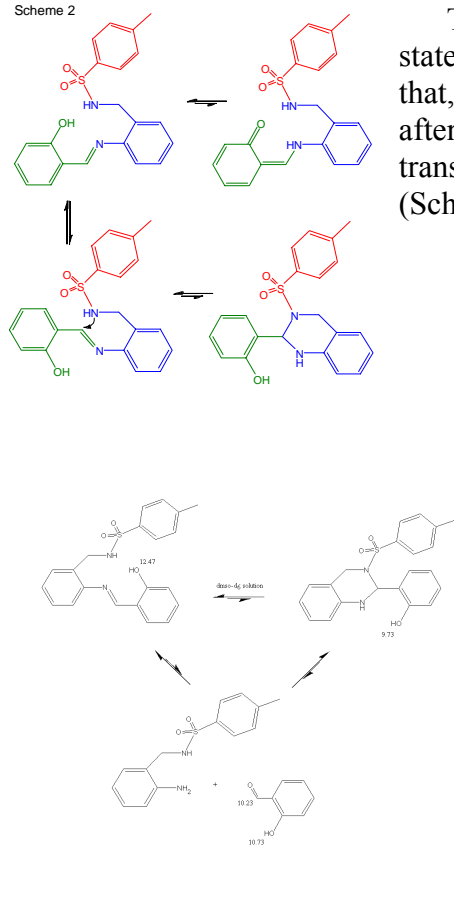
Geometric parameters do not merit further comment, as they are in the typical ranges found for related compounds [1,3].

The molecular structure (Fig. 1) shows an *E* configuration in the azomethine group, with a typical intramolecular H bond between the phenol and the imine groups.

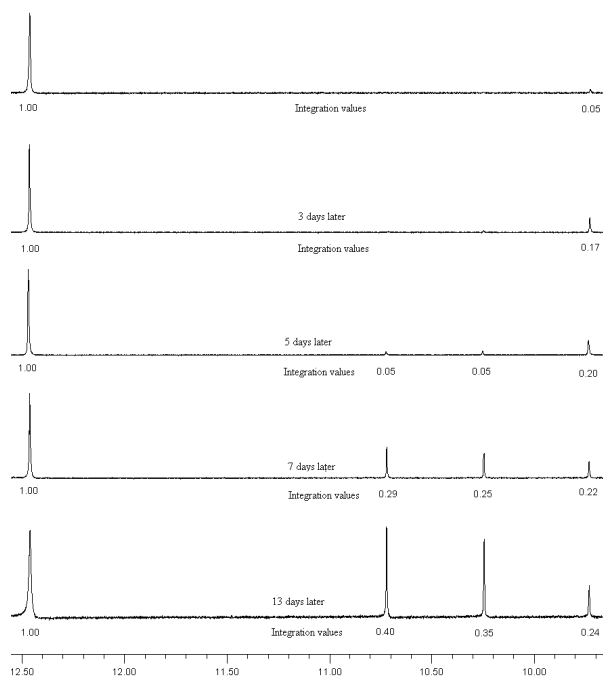
In this particular case, both crystal data at 100 K, and H bonding scheme clearly correspond to a hydroxyimine tautomer (Scheme 2). However, some character of ketoamine can be reflected by the distance of 1.350(3) Å between C20 and O3 (Fig. 1), which seems some short for a pure C-O simple bond.



Scheme 2



The compound is air and light stable in the solid state, but an NMR experiment not only demonstrated that, the compound had suffered some decomposition after two weeks, but it also experimented some transformation into a tetrahydroquinazoline derivative (Scheme 2).



Experimental procedure

Salicylaldehyde (0.154 g, 1.45 mmol) were added to a chloroform solution (60 mL) of *N*-(2-aminobenzyl)-4-methylbenzenesulfonamide (0.400 g, 1.45 mmol). The resulting solution was refluxed for 24 h. After cooling, it was filtrated upon celite, and the resulting solution was concentrated to obtain an oily solid, which after stirred with hexane yields a yellow solid (0.496 g, 90%), subsequently characterised as **I**. Recrystallisation both in EtOH and CHCl_3 allowed the isolation of yellow prismatic single crystals of **I**, which were suitable for X-ray diffraction studies.. Mp: 190-192 °C. Calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$ (380.46 g/mol): C, 66.29; H, 5.30; N, 7.36%. Found: C, 65.75; H, 5.55; N, 7.48 %. MS (FAB): m/z 381.2 [M^+ , 100%]. IR (KBr, v/cm^{-1}): 1616 (C=N), 1382 ($\text{SO}_2_{\text{asim}}$) 1163 ($(\text{SO}_2_{\text{sim}})\text{OH}$). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ = 12.47 (1H, OH), 8.74 (1H, CH=N), 8.03 (1H, NH), 6.97-7.65 (4H arom_{sal}) 7.22-7.38 (4H, arom_{amine}), 7.31-7.64 (4H, arom_{Ts}), 4.08 (2H, CH_2), 2.35 (3H, CH_3). Crystal data for **I**: (at 100(2) K): triclinic, *P*-1 (No. 2), $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$, $M_w = 380.45$, $a = 7.4502(3)$, $b = 11.1160(5)$, $c = 11.7738(5)$ Å, $\alpha = 74.955(2)$, $\beta = 106.879(5)$, $\gamma = 73.140(2)$ °. $V = 900.76(7)$ Å³, $Z = 2$; $\rho_{\text{calc}} = 1.403$ g·cm⁻³; $R_1 = 0.0537$ and $wR_2 = 0.1029$ ($I > 2\sigma I$), residual electron density 0.311 e⁻ Å³.

References

- [1] J. Sanmartín, F. Novio, A. M. García-Deibe, M. Fondo, M. R. Bermejo, *New J. Chem.*, **2007**, *31*, 1605.
- [2] J. Sanmartín, F. Novio, A. M. García-Deibe, M. Fondo, N. Ocampo, M. R. Bermejo, *Eur. J. Inorg. Chem.*, **2008**, 1719.
- [3] P. A. Vigato and S. Tamburini, *Coord. Chem. Rev.* 2004, **248**, 1717.