SHORT PAPER

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Evidence of proton transfer from the hydroxy O atom to the imine N atom, crystal structure of N-salicylideneamine-1-tris(hydroxymethyl)methane†

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The structural study of the Schiff base compound, *N*-salicylideneamine-1-tris(hydroxymethyl)-methane, confirmed that the hydroxy H atom has transferred to the imine N atom with the intramolecular O…N bond being 2.6215(19) Å.

It is well known that Schiff bases are frequently used as ligands in the formation of transition metal complexes. Many such complexes[1] have been structurally characterised by X-ray crystallography but only a few free Schiff base compounds have been structurally characterised.[2-5] *N*-Substituted salicylaldimines have been reported to display thermochromism and photochromism in the solid state by proton transfer from the hydroxy O atom to the imine N atom.[5,6] This change is reversible and the charge-transport occurs *via* overlapping intra-molecular π orbitals along with the proton transfer. It is also suggested that proton oscillation between the O and N atoms may be applied to the development of molecular devices.[5]

Among the structurally reported free Schiff bases, the proton is covalently bonded to the hydroxy O atom rather than the imine N atom but does hydrogen bond to the N atom. Our structural investigation of the Schiff base compound, *N*-salicylideneamine-1-tris(hydroxy)methyl-methane, confirm that the H atom is covently bonded to the N atom and hydrogen bonded to the O atom as shown in Fig.1. Preparation of the compound was easily achieved by mixing equivalent amounts of salicylaldehyde and tris(hydroxymethyl)aminomethane in ethanol in high yield (>95%). Elemental analysis of the compound for C, H, and N agrees well with the calculated values. In the X-ray crystallographic study, the H atom was located from the difference Fourier map at the end of the refinement process as a small positive electron density, other H atoms were located using a riding mode and they were refined isotropically. The strong hydrogen interaction is observed with the O…N distance being 2.6215(19) Å. The sum of the van der Waals radii of O and N (3.07 Å)[7] is significantly longer than the O…N hydrogen-bond distance, which is similar to the corresponding hydrogen bonding O…N distances in *N*-(2-hydroxyphenyl)- salicylaldimine [2.625(7) Å],[3] 2,2'-azinodimethyldiphenol [2.611(6) Å][4] and bis-*N*,*N'*-p-chlorosalideneamine-1,2-diaminobenzene [2.615(6) Å].[5] The N=C7 bond distance of 1.299(2) Å is somewhat longer that found in 2-salicylideneamino-4,5,6,7-tetrahydrobenzo-[*b*]thiophene-3-carbonitrile [1.281(2) Å][2] but similar to that in *N*-(2-hydroxy-4-chloro-phenylmethyl)- salicylaldimine [1.297(5) Å].[8] IR spectrum absorption peak at 1634 cm^{-1} is characteristic of the double bond. The N–H and H…O1 distances are 1.01 and 1.77 Å, respectively. The N–H…O1 angle is 139.8(18)°. Apart from the intramolecular hydrogen bond, there are several intermolecular hydrogen bonds as shown in Fig.2. The O1 atom accepts two other H atoms from the alcoholic groups of the adjacent molecule with O1…O3i and O1…O4i (i: *x*, 0.5–*y*, 0.5+*z*) distances being 2.7362(19) and 2.6501(18) Å, respectively. The O2…O4ii (ii: –*x*, 1–*y*, 2–*z*) distance is 2.7331(19) Å.

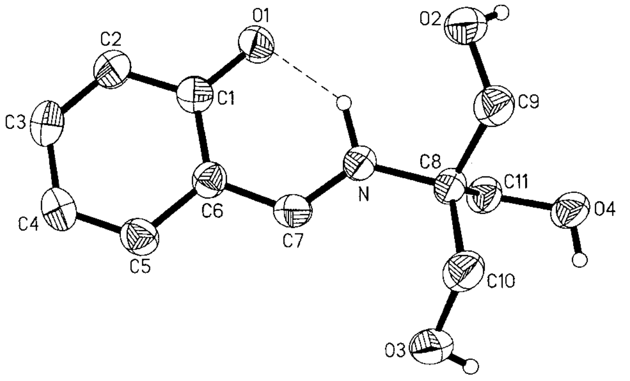

Fig. 1 X-ray crystal structure of *N*-salicylideneamine-1-tris(hydroxymethyl)-methane.

The compound is water soluble. It can also dissolve in acetone, DMSO, MeCN, MeOH, and EtOH, but does not dissolve in methylene dichloride, chloroform, and benzene. ^{1}H NMR spectral data for the compound in CD_3CN shows that there is a peak at 8.64 ppm which is attributed to the H atom of –CH=N– group. Peaks around 6.86 ppm are attributed to H atoms at *p*- and *o*-positions of the phenyl group relative to the phenol O atom. Peaks around 7.33 ppm are attributed to *m*-position H atoms. A strong double peak at 3.75 ppm can be assigned to CH_2 groups. Two other peaks at 3.27 and 3.04 ppm can be attributed to the H atoms of OH groups. The H atom may oscillate between the phenolic O atom and the Schiff base N atom in solution.

Experimental

Elemental analysis was carried out on a 240C analyser. ^{1}H NMR spectra were recorded with Varian VXR 300MHz spectrometer. IR spectra were recorded on a Nicolet Nexus 470 FT-IR spectrophotometer, KBr disc. A Shimadzu 2101 UV-vis scanning spectrophotometer was used to record the UV-vis spectrum.. Melting point measurement was carried out using a Fisher digital melting point analyzer Model 355.

Synthesis of the title compound: To a solution of salicylaldehyde (10mmol, 1.22g) in 15 ml ethanol was added a solution of tris(hydroxymethyl) aminomethane (10 mmol, 1.21g) in 5 ml water. The mixture was stirred at room temperature for 1 h. The resulting yellow solution was filtered and good-shaped crystals were obtained after 2 days. Yield: 2.27 g (95.5%) (Found; C, 58.24; H, 6.82; N, 6.30. $C_{11}H_{15}NO_4$ requires C, 58.65; H, 6.71; N, 6.22; m.p. = 149–150 °C). ν_{max}/ cm^{-1} 1634.21(s, C=N), 1608.22(s), 1555.96(w), 1536.36(s), 1513.85(w), 1487.47(s), 1456.22(m), 1418.47(w), 1395.76(m), 1365.62(w), 1306.63(s), 1279.20(w), 1226.00(s), 1189.67(m), 1153.54(s), 1132.00(m), 1101.39(m), 1059.60(s), 1028.71(s), 982.50(m), 934.49(w), 919.78(w), 893.66(m),871.10(w), 800.35(w), 777.15(w), 765.37(s),737.32(m). δ_H [CD_3CN] 8.64

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

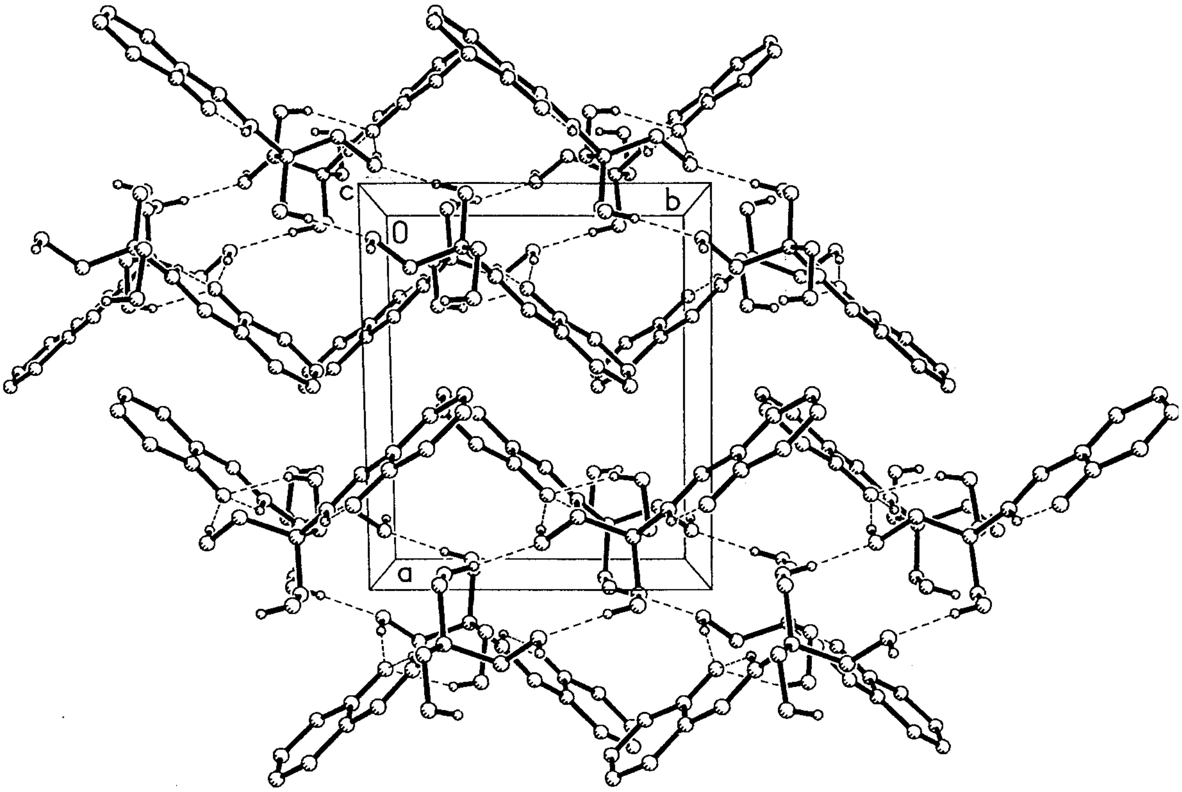

Fig. 2 Crystal packing of the Schiff base compound.

(s, 1H, –CH=N–), 7.41 (d, 1H, 3-H of phenyl), 7.34 (t, 1H, 5-H of phenyl), 6.8 (m, 2H, 4,6-phenyl)3.75 (d, 6H, CH_2). The UV-vis spectrum of the compound shows five peaks (EtOH, 0.71035×10^{-4} mol/l): 400.5nm (ε, 2.95×10^3), 317.0nm (ε, 2.73×10^3) 276.0nm (ε, 5.95×10^3), 251.0nm (ε, 9.77×10^3), 215nm (ε, 2.074×10^4).

Crystal data: $C_{11}H_{15}NO_4$, $M_r = 225.24$, $F(000) = 480$, yellow crystal, monoclinic system, $a = 10.498(2)$, $b = 8.718(1)$, $c = 12.642(2)$ Å, $\beta = 101.64(2)°$, $U = 1133.2$ Å^3, space group $P2_1/c$, $Z = 4$, $Dc = 1.320$ g cm^{-3}, μ = (Mo-Kα) = 1.01 cm^{-1}.

The data were collected at a temperature of 25°C on a Bruker P4 diffractometer with Mo–Kα radiation (λ = 0.71073 Å) and the ω-2θ scan technique to a maximum 2θ value of 50° [$-1 \le h \le 12$, $-1 \le k \le 10$, $-15 \le l \le 14$].

The structure was solved by direct methods (SHELXS 97).[9] The non-hydrogen atoms were refined anisotropically (SHELXL 97).[10] Hydrogen atoms bonded to carbon atoms were located using the riding mode, other hydrogen atoms were located from the difference Fourier map and were refined isotropically. The final cycle of full-matrix least-squares refinement wasbased on 1232 observed reflections [$I > 2\sigma(I)$] and 153 variable parameters and converged to $R = 0.0361$ and $Rw = 0.0809$. The weighting scheme, $w = 1 / [\sigma^2(Fo^2) + (0.0459P)^2]$ where $P = (Fo^2 + 2Fc^2)/3$, was found to give satisfactory analysis of the variance.

Data collection: XSCANS (Siemens, 1991),[11] Cell refinement: XSCANS.[11] Data reduction: SHELXTL-Plus (Sheldrick, 1990).[12] Molecular graphics: SHELXTL-Plus.[12]

§ Full crystallographic details, excluding structure factors, have been deposited with the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research (S).* 1999, Issue 1. Any request to the CCDC for this matrial should quote the full literature citation and the reference number.

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