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The structures of some *ortho*-hydroxy Schiff base ligands

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Abstract

Nine *ortho*-hydroxy Schiff base ligands, (**1**)–(**9**), were synthesized and characterized by chemical analysis, mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy. The crystal and molecular structures of compounds (**1**), (**3**), (**5**), (**7**), (**8**) and (**9**) were determined. The solid state X-ray diffraction studies show that compounds (**5**) and (**8**) are in the keto–amine tautomeric form, while (**1**), (**3**), (**7**) and (**9**) are found as phenol–imine tautomers. Moreover, studies in the solution phase by ^{1}H and ^{13}C NMR spectroscopy indicate that compounds (**2**), (**5**) and (**8**) are found as keto–amine tautomers, while (**1**), (**3**), (**4**), (**6**), (**7**) and (**9**) are found as phenol–imine tautomers. Furthermore, ab initio calculations at the HF/6-31G* level with full optimization of geometry, performed for both tautomers of (**1**) and (**5**), agree with the observed behavior in solution and solid state of these compounds.

Keywords: Crystal structure of *o*-hydroxy Schiff base ligands; ^{1}H and ^{13}C NMR studies of *o*-hydroxy Schiff bases; Tautomerism in *o*-hydroxy Schiff bases; Ab initio calculations of *o*-hydroxy Schiff bases; Synthesis of Schiff bases

1. Introduction

There has been considerable interest in some Schiff bases derived from salicylaldehyde because they show thermochromism and photochromism in the solid state [1–3]. It has been proposed that molecules showing thermochromism are planar, while those showing photochromism are non-planar [4,5], both phenomena being associated with a proton transfer [5,6]. Consequently, it is evident that a closely related phenomenon of interest is the possibility of tautomeric isomerism in *ortho*-hydroxy Schiff bases. In particular, we are interested in comparing those derived from salicylaldehyde with those from 2-hydroxy-1-naphthaldehyde and 3-hydroxy-2-naphthaldehyde, where there are intrinsic aromaticity differences that could be reflected in some structural features of these ligands. Therefore, the structures of this kind of Schiff bases, which are widely used as chelating agents, are relevant due to the possibility of finding them in the solid state and/or in solution as keto–amine or phenol–imine tautomers, and their connections with photochromism and thermochromism. Furthermore, there are only a small number of structures determined by X-ray crystallography for 1,2-naphthalenic Schiff bases [7–13] and an even smaller number for 2,3-naphthalenic Schiff bases [14].

In this paper, we report the characterization of several Schiff base ligands resulting from the condensation of: salicylaldehyde, 2-hydroxy-1-naphthaldehyde and 3-hydroxy-2-naphthaldehyde with 1-adamantanamine, cyclohexylamine and

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1-adamantanemethylamine, respectively, i.e. *N*-(1-adamantyl)-salicylaldamine (**1**) [15], 1-[(1-adamantylamino)-methylene]2-(1*H*)-naphthalenone (**2**) [15], whose crystal structure has already been studied [7], 2-[(1-adamantyl)iminomethyl]-3-naphthol (**3**) [15], *N*-(cyclohexyl)-salicylaldamine (**4**), 1-[(cyclohexylamino)methylene]-2-(1*H*)-naphthalenone (5) [16], 2-[(cyclohexyl)iminomethyl]-3-naphthol (**6**) [16], *N*-(1-adamantanemethyl)-salicylaldamine (**7**), 1-[(1-adamantanemethylamino)methylene]-2-(1*H*)-naphthalenone (**8**) and 2-[1-(adamantanemethyl)-iminomethyl]-3-naphthol (**9**). The crystal and molecular structure of compounds (**1**), (**3**), (**5**), (**7**), (**8**) and (**9**) were determined. Although some ^{1}H NMR spectroscopic characteristics of compounds (**1**), (**2**), (**3**), (**5**) and (**6**) have already been reported [15,16], this study allow us to make a more correct assignment of their NMR signals and their structures in solution.

While it has been reported that in the solid state some Schiff bases derived from 2-hydroxy-1-naphthaldehyde and *n*-propyl- and *n*-butylamine, respectively [8,9], are found as phenol–imine tautomers, the data obtained here suggest that in the crystalline state as well as in solution, the keto–amine tautomer prevails in Schiff bases resulting from the condensation of 2-hydroxy-1-naphthaldehyde and alkylamines, while those Schiff bases derived from salicylaldehyde or 3-hydroxy-2-naphthaldehyde and alkylamines are mainly found as phenol–imine tautomers.

In relation to the theoretical calculations, it has been found that the keto tautomer is the preferred one by almost 48 kJ/mol for acetone [17], but, there are certain cases where the enol form can be stabilized [18]. Indeed, the presence of aromaticity against a quinoid form allows the equilibrium to be shifted to the side of the enol. This is the case where an MP2/6-31G*//RHF-6-31G* result shows a ΔGT of 70.61 kJ/mol [19], for the equilibrium from phenol to 2,5-cyclohexadienone and 72.5 kJ/mol from phenol to 2,4-cyclohexadienone. However, in the case of substituted 2-naphthols, when there is an imine group at position 1 of the naphthalene ring, the tautomeric equilibrium between the keto form and the enol form seems to be more constricted than other aryl–enol cases because in both tautomers a strong hydrogen bond is present, and in the keto–amine isomer the double bond formed between the C1 atom of the ring and the C atom of the lateral chain gives an interesting resonant form to the molecule in such a way that the energy of both tautomers would be very close.

2. Experimental

2.1. Reagents and techniques

Cyclohexylamine, 1-(aminomethyl)adamantane, 1-adamantanamine, 2-hydroxy-1-naphthaldehyde and salicylaldehyde were obtained from Aldrich Chemical Co. Inc., and were used without further purification; 3-hydroxy-2-naphthaldehyde was prepared from naphthol AS (Aldrich) as described [20]. Melting points were determined in a Fisher–Jones apparatus and are uncorrected; mass spectra were obtained using a JEOL Mod. JMS-SX-102A mass spectrometer operated at 70 eV ionizing potential. All the NMR data were acquired on a Varian UNITY 300 spectrometer equipped with a four-channel nucleus probe or/and a Varian Unity 500 spectrometer equipped with a two-nucleus inverse detection probe operating at 300 K. Samples of 60 mg were dissolved in ca. 0.7 ml of $CDCl_3$ in a 5 mm tube using $CDCl_3$ and TMS as internal standard. COSY [21], absolute intensity spectra were recorded for a ^{1}H spectral width of 2600 Hz with 1024 data points (zero-filled to 2048), 256 increments and 16 transients per increment. Zero-filled to 512 and Gaussian weighting were used in both dimensions. For NOESY spectra [22], the same spectral width and processing parameters as for the COSY spectra were used with mixing times of 1.2 s.

HETCOR spectra [23,24] had identical ^{1}H parameters, while the ^{13}C window was 10,700 Hz and 128 time increments were collected (128 transients per increment). Gaussian weighting was applied in both dimensions.

Spectral widths of 2600 Hz were used for ^{1}H, while 13,250 Hz for ^{13}C spectral width. 128 time increments (with 256 transients per increment) in the second dimension and linear predicted to 256 increments for the FLOCK spectra [25] were used. Gaussian weighting functions were applied in the latter. All assignments shown in Table 3 were performed using ^{1}H, ^{13}C, DEPT, HETCOR, FLOCK and NOESY spectra.

Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, TN, USA.

Table 1
Crystallographic data for compounds (**1**), (**3**), (**5**), (**7**), (**8**) and (**9**)

	Compound					
	(**1**)	(**3**)	(**5**)	(**7**)	(**8**)	(**9**)
Empirical formula	$C_{17}H_{21}NO$	$C_{21}H_{23}NO$	$C_{17}H_{19}NO$	$C_{18}H_{23}NO$	$C_{22}H_{25}NO$	$C_{22}H_{25}NO$
Color, habit	Yellow, lamina	Yellow, block	Orange, irregular	Yellow, prism	Yellow, prism	Orange, prism
Formula weight	255.35	305.41	253.33	269.37	319.43	319.43
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073 (MoKα)	0.71073 (MoKα)	0.71073 (MoKα)	1.54178 (CuKα)	0.71073 (MoKα)	1.54178 (CuKα)
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P-1$	$Pna2_1$	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Unit cell dimensions	$a = 6.5090(1)$ Å	$a = 30.482(6)$ Å	$a = 8.485(2)$ Å	$a = 6.502(1)$ Å	$a = 6.784(1)$ Å	$a = 6.452(1)$ Å
	$b = 9.4780(1)$ Å	$b = 17.217(4)$ Å	$b = 12.037(3)$ Å	$b = 21.900(4)$ Å	$b = 15.429(1)$ Å	$b = 11.380(2)$ Å
	$c = 12.3690(1)$ Å	$c = 6.431(3)$ Å	$c = 13.827(3)$ Å	$c = 10.508(2)$ Å	$c = 16.344(2)$ Å	$c = 23.300(5)$ Å
	$\alpha = 94.400(1)°$	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 103.290(1)°$	$\beta = 90°$	$\beta = 90°$	$\beta = 91.71(3)°$	$\beta = 98.98(1)°$	$\beta = 97.89(3)°$
	$\gamma = 104.070(1)°$	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$
Volume (Å^3)	713.21(14)	3375.0(19)	1412.2(6)	1495.6(5)	1689.8(3)	1694.6(5)
Z	2	8	4	4	4	4
Density (calcd) (Mg m^{-3})	1.189	1.202	1.192	1.196	1.256	1.252
Absorption coefficient	0.073 mm^{-1}	0.073 mm^{-1}	0.073 mm^{-1}	0.564 mm^{-1}	0.076 mm^{-1}	0.583 mm^{-1}
$F(000)$	276	1312	544	584	688	688
Crystal size (mm)	$0.8 \times 0.44 \times 0.36$	$0.44 \times 0.4 \times 0.28$	$0.6 \times 0.4 \times 0.24$	$0.6 \times 0.44 \times 0.26$	$0.4 \times 0.24 \times 0.22$	$0.4 \times 0.16 \times 0.1$
Diffractometer	Siemens P4	Siemens P4	Siemens P4	Siemens P3/F	Siemens P4	Siemens P3/F
θ Range for data collection	1.5–25	1.5–25	1.5–27.5	1.5–55	1.5–27.5	1.5–55
Scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	ω	$\theta/2\theta$
Index ranges	$0 \le h \le 7$	$-1 \le h \le 36$	$0 \le h \le 11$	$0 \le h \le 6$	$0 \le h \le 8$	$0 \le h \le 6$
	$-11 \le k \le 10$	$-20 \le k \le 1$	$0 \le k \le 15$	$0 \le k \le 23$	$0 \le k \le 20$	$0 \le k \le 12$
	$-14 \le l \le 14$	$-1 \le l \le 7$	$-17 \le l \le 17$	$-11 \le l \le 11$	$-21 \le l \le 20$	$-24 \le l \le 24$
Absorption correction	N/A	N/A	N/A	N/A	N/A	N/A
Reflections collected	2735	4266	3581	2067	4193	2361
Independent reflections	2495	3840	3228	1875	3873	2129
$R_{(int)}$	0.0428	0.0410	0.0802	0.0846	0.0243	0.0412
Data/restraints/parameters	2495/0/176	3840/1/422	3228/0/176	1875/0/185	3873/0/221	2129/0/221
Goodness-of-fit on F^2	1.165	1.030	1.005	1.066	1.001	1.027
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.058$, $wR_2 = 0.1792$	$R_1 = 0.071$, $wR_2 = 0.1663$	$R_1 = 0.066$, $wR_2 = 0.1276$	$R_1 = 0.0395$, $wR_2 = 0.1032$	$R_1 = 0.0634$, $wR_2 = 0.1234$	$R_1 = 0.0432$, $wR_2 = 0.099$
Largest diff. peak and hole (eÅ^{-3})	1.34 and −0.152	0.305 and −0.193	0.122 and −0.134	0.125 and −0.131	0.186 and −0.162	0.120 and −0.140

2.2. Synthetic procedures

The Schiff base ligands (**1**)–(**9**), were prepared by a literature method [26]. The general method is as follows:

To a solution of aldehyde (0.004 mol) in ethanol (100 ml) was added a solution of amine (0.004 mol) in ethanol (75 ml). The resulting solution was boiled under reflux for ca. 4 h, then concentrated and cooled in an ice bath until crystallization was observed. The yellow solid was suction filtered, dried and recrystallized from dichloromethane–methanol.

*N-(1-Adamantyl)-salicylaldamine (**1**)* [15]. Yellow crystals, m.p. 82–84°C; M^+ 255 *m/z* (base peak 135 *m/z*). Found: C, 79.84; H, 8.24; N, 5.53%. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.30; N, 5.49%.

*1-[(1-Adamantylamino)methylene]-2-(1H)-naphthalenone (**2**)* [15]. Yellow crystals, m.p. 165–166°C; M^+ 305 *m/z* (base peak 305 *m/z*). Found: C, 82.47; H, 7.62; N, 4.56%. Calcd for $C_{21}H_{23}NO$: C, 82.57; H, 7.59; N, 4.59%.

*2-[(1-Adamantyl)iminomethyl]-3-naphthol (**3**)* [15]. Yellow crystals, m.p. 155–156°C; M^+ 305 *m/z* (base peak 305 *m/z*). Found: C, 82.49; H, 7.56; N, 4.55%. Calcd for $C_{21}H_{23}NO$: C, 82.57; H, 7.59; N, 4.59%.

*N-(Cyclohexyl)-salicylaldamine (**4**).* Pale yellow liquid, b.p. 85°C (1 mmHg); M^+ 203 *m/z* (base peak 203 *m/z*). Found: C, 76.82; H, 8.50; N, 6.95%. Calcd for $C_{13}H_{17}NO$: C, 76.79; H, 8.43; N, 6.89%.

*1-[(Cyclohexylamino)methylene]-2-(1H)-naphthalenone (**5**)* [16]. Yellow crystals, m.p. 68–70°C; M^+ 253 *m/z* (base peak 170 *m/z*). Found: C, 80.51; H, 7.61; N, 5.56%. Calcd for $C_{17}H_{19}NO$: C, 80.58; H, 7.56; N, 5.53%.

*2-[Cyclohexyliminomethyl]-3-naphthol (**6**)* [16]. Pale yellow crystals, m.p. 126–128°C; M^+ 253 *m/z* (base peak 253 *m/z*). Found: C, 80.61; H, 7.54; N, 5.55%. Calcd for $C_{17}H_{19}NO$: C, 80.58; H, 7.56; N, 5.53%.

*N-(1-Adamantanemethyl)-salicylaldamine (**7**).* Yellow crystals, m.p. 91–92°C; M^+ 269 *m/z* (base peak 135 *m/z*). Found: C, 80.15; H, 8.53; N, 5.17%. Calcd for $C_{18}H_{23}NO$: C, 80.24; H, 8.61; N, 5.20%.

*1-[(1-Adamantanemethylamino)methylene]-2-(1H)-naphthalenone (**8**).* Yellow crystals, m.p. 200–201°C; M^+ 319 *m/z* (base peak 319 *m/z*). Found: C, 82.64; H, 7.85; N, 4.37%. Calcd for $C_{22}H_{25}NO$: C, 82.70; H, 7.89; N, 4.39%.

*2-[1-Adamantanemethyl)iminomethyl]-3-naphthol (**9**).* Yellow crystals, m.p. 172–174°C; M^+ 319 *m/z* (base peak 319 *m/z*). Found: C, 82.72; H, 7.85; N, 4.40%. Calcd for $C_{22}H_{25}NO$: C, 82.76; H, 7.89; N, 4.39%.

2.3. Crystallography

Good-quality crystals suitable for the X-ray diffraction study were obtained by slow layer diffusion of methanol into a saturated dichloromethane solution of compounds (**1**), (**3**), (**5**), (**7**), (**8**) and (**9**) at room temperature.

2.3.1. Data collection and processing

All crystals were mounted on glass fibers. Preliminary examinations and data collection for (**1**), (**3**), (**5**), and (**8**) were performed on a Siemens P4/PC diffractometer (MoKα radiation, oriented graphite monochromator), and for (**7**) and (**9**) on a Siemens P3/F diffractometer (CuKα radiation, oriented graphite monochromator) at 293(2) K. Cell parameters were calculated from the least-squares fitting for 25 high-angle reflections. Omega scans for several intense reflections indicated acceptable crystal quality. Data were collected for 3.00–50.00° using a two-theta scan mode at 293(2) K with a variable scan rate. Three standards were collected for every 97 reflections showing no significant trends. Background measurements were done by stationary crystal and stationary counter techniques at the beginning and the end of each scan for half the total scan time. Lorentz and polarization corrections were applied to the data set and only unique reflections were used in further calculations (see Table 1).

2.3.2. Structure solution and refinement

The structures were solved by Direct Methods [27]. Anisotropic full-matrix least-squares refinement [28] on F^2 was done for all non-Hydrogen atoms. Weighted *R*-factors, *wR*, and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > 2\sigma(F^2)$ are used only for calculating *R* factors. Hydrogen atoms attached to C atoms were placed in idealized positions with isotropic thermal

Table 2
Selected bond lengths (Å) and angles (°) for compounds (**1**), (**3**), (**5**), (**7**), (**8**) and (**9**)

Compound (**1**)			
C(1)–C(2)	1.401(4)	N(1)–C(7)–C(1)	121.8(3)
C(2)–C(3)	1.390(4)	O(1)–C(2)–C(1)	121.0(3)
C(3)–C(4)	1.369(5)	C(7)–N(1)–C(8)	122.9(2)
C(1)–C(7)	1.460(4)	O(1)–C(2)–C(3)	119.4(3)
O(1)–C(2)	1.352(4)	C(1)–C(2)–C(3)	119.6(3)
N(1)–C(7)	1.269(3)	C(2)–C(3)–C(4)	119.8(3)
N(1)–C(8)	1.473(3)	C(2)–C(1)–C(7)	121.5(3)
Compound (**3**)			
C(1a)–C(2a)	1.356(10)	N(1a)–C(11a)–C(2a)	121.9(8)
C(2a)–C(3a)	1.427(11)	O(1a)–C(3a)–C(2a)	121.6(7)
C(3a)–C(4a)	1.373(10)	C(11a)–N(1a)–C(12a)	124.3(7)
C(2a)–C(11a)	1.472(10)	O(1a)–C(3a)–C(4a)	118.8(8)
O(1a)–C(3a)	1.358(9)	C(1a)–C(2a)–C(3a)	119.2(7)
N(1a)–C(11a)	1.270(9)	C(2a)–C(3a)–C(4a)	119.6(7)
N(1a)–C(12a)	1.461(9)	C(3a)–C(2a)–C(11a)	120.7(7)
C(1b)–C(2b)	1.372(11)	N(1b)–C(11b)–C(2b)	121.9(8)
C(2b)–C(3b)	1.436(12)	O(1b)–C(3b)–C(2b)	119.5(8)
C(3b)–C(4b)	1.370(11)	C(11b)–N(1b)–C(12b)	121.8(7)
C(2b)–C(11b)	1.478(10)	O(1b)–C(3b)–C(4b)	122.1(9)
O(1b)–C(3b)	1.364(10)	C(1b)–C(2b)–C(3b)	119.6(8)
N(1b)–C(11b)	1.296(10)	C(2b)–C(3b)–C(4b)	118.4(8)
N(1b)–C(12b)	1.470(10)	C(3b)–C(2b)–C(11b)	121.8(8)
Compound (**5**)			
C(1)–C(2)	1.435(5)	N(1)–C(11)–C(1)	124.1(3)
C(2)–C(3)	1.445(5)	O(1)–C(2)–C(1)	122.9(3)
C(3)–C(4)	1.339(5)	C(11)–N(1)–C(12)	123.4(3)
C(1)–C(11)	1.403(4)	O(1)–C(2)–C(3)	120.4(3)
O(1)–C(2)	1.263(4)	C(1)–C(2)–C(3)	116.6(3)
N(1)–C(11)	1.310(5)	C(2)–C(3)–C(4)	122.1(3)
N(1)–C(12)	1.474(4)	C(2)–C(1)–C(11)	118.9(3)
Compound (**7**)			
C(1)–C(2)	1.402(2)	N(1)–C(7)–C(1)	122.87(14)
C(2)–C(3)	1.392(2)	O(1)–C(2)–C(1)	121.33(15)
C(3)–C(4)	1.375(3)	C(7)–N(1)–C(8)	119.22(14)
C(1)–C(7)	1.454(2)	O(1)–C(2)–C(3)	119.02(15)
O(1)–C(2)	1.350(2)	C(1)–C(2)–C(3)	119.64(16)
N(1)–C(7)	1.270(2)	C(2)–C(3)–C(4)	119.99(17)
N(1)–C(8)	1.458(2)	C(2)–C(1)–C(7)	121.00(14)
Compound (**8**)			
C(1)–C(2)	1.423(4)	N(1)–C(11)–C(1)	123.5(3)
C(2)–C(3)	1.440(4)	O(1)–C(2)–C(1)	122.9(3)
C(3)–C(4)	1.347(4)	C(11)–N(1)–C(12)	124.5(3)
C(1)–C(11)	1.410(4)	O(1)–C(2)–C(3)	122.9(3)
O(1)–C(2)	1.285(3)	C(1)–C(2)–C(3)	118.2(3)
N(1)–C(11)	1.303(3)	C(2)–C(3)–C(4)	121.1(3)
N(1)–C(12)	1.459(3)	C(2)–C(1)–C(11)	118.3(2)
Compound (**9**)			
C(1)–C(2)	1.372(3)	N(1)–C(11)–C(2)	121.5(2)
C(2)–C(3)	1.428(3)	O(1)–C(3)–C(2)	120.3(2)
C(3)–C(4)	1.370(3)	C(11)–N(1)–C(12)	121.5(2)
C(2)–C(11)	1.458(3)	O(1)–C(3)–C(4)	119.7(2)
O(1)–C(3)	1.358(2)	C(1)–C(2)–C(3)	118.5(2)
N(1)–C(11)	1.274(3)	C(2)–C(3)–C(4)	120.0(2)
N(1)–C(12)	1.468(3)	C(3)–C(2)–C(11)	120.6(2)

parameters fixed 1.2 times the value of the attached atom. The H atoms attached to N or O atoms were located on a difference Fourier map at an advanced stage of refinement and their positional parameters refined. Neutral atom scattering factors and anomalous scattering factors were taken from the International Tables for X-ray Crystallography [29].

Theoretical calculations were carried out using the GAUSSIAN-94 program [30] at the HF/6-31G* level with full optimization of geometry. The initial geometries were built using the Universal 1.01 Molecular Mechanics software [31]. Both methods mentioned above are included in the Cerius package.[1]

3. Results and discussion

3.1. Crystal study

Crystal data, additional data collection parameters and refinement details are given in Table 1. A selection of bond lengths and angles is given in Table 2. The molecular structures of (**1**), (**3**), (**5**), (**7**), (**8**) and (**9**), including atom-numbering schemes, are illustrated in Figs. 1–6.

In the unit cell of compound (**3**), there are two crystallographically independent but structurally very similar molecules, (**3a**) and (**3b**), differing only in the rotational orientation of the 1-adamantyl group in relation to the rest of the molecule.

Compounds (**1**), (**3a**), (**3b**), (**7**) and (**9**) crystallize in the solid state into the phenol–imine tautomeric form with O–H distances of 0.86(4), 0.86(9), 0.97(10), 0.94(2), and 1.03(2) Å, respectively. Strong intramolecular hydrogen bonds occur between the O1 and N1 atoms, with N···H distances of 1.79(4), 1.82(10), 1.76(11), 1.74(2) and 1.62(2) Å,

[1] The results published were generated using the program CERIUS^{2}™, developed by Molecular Simulations Inc.

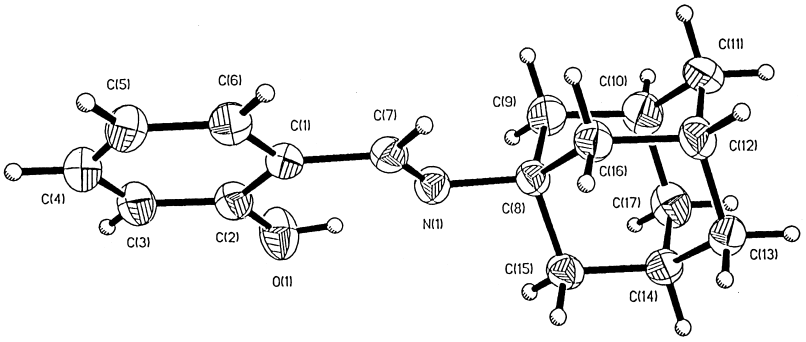

Fig. 1. Molecular structure of compound (**1**) in the solid state with the atom numbering scheme. Thermal ellipsoids are drawn at 50% of probability.

respectively, while N···O distances are 2.594(3), 2.618(9), 2.618(10), 2.6041(18) and 2.563(2) Å, respectively; the values for the O–H···N angles are 155(4), 153(9), 147(9), 151(2) and 151(2)°, respectively.

The range of C–O bond lengths (1.352(4)–1.364(10) Å) correspond to the value described for the C–O bond in phenols (1.362 Å) [32], while the ranges for C=N bonds (1.270(9)–1.296(10) Å) and the bond lengths between the C1 atom of the aromatic rings and the C atom of the imine groups (1.454(2)–1.478(10) Å) correspond to conjugated C=N groups (1.279 Å) and Car–C=N– bond lengths (1.476(14) Å) [32], respectively.

In contrast, for compounds (**5**) and (**8**), which are structurally very similar, the tautomeric keto–amine isomer is observed with N–H distances of 0.92(4) and 0.89(3) Å, respectively. Strong intramolecular hydrogen bonds are found between the N1 and O1 atoms with O···H distances of 1.84(4) and 1.76(3) Å, respectively, while N···O distances are

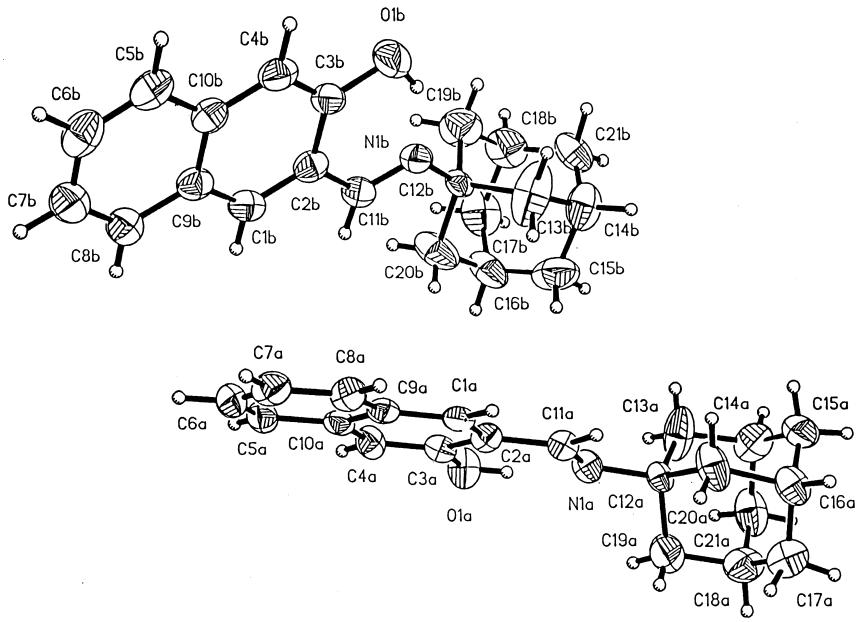

Fig. 2. Molecular structure of the two molecules of compound (**3**) in the solid state with the atom numbering scheme. Thermal ellipsoids are drawn at 50% of probability.

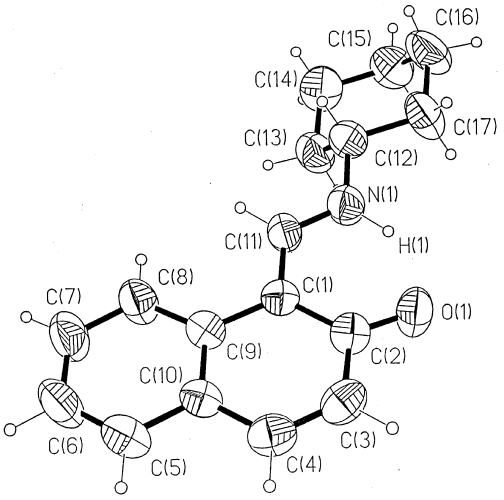

Fig. 3. Molecular structure of compound (**5**) in the solid state with the atom numbering scheme. Thermal ellipsoids are drawn at 50% of probability.

2.587(4) and 2.540(3) Å, respectively; the values for the N–H···O angles are 136(3) and 146(3)°, respectively. The bond lengths of the fragment N1–C11–C1–C2–O1 suggest an electronic delocalization, i.e. the C2–O1 bond lengths, 1.266(4) and 1.285(3) Å, are similar to the values observed for conjugated C=O bonds. The C1–C2 bond length values are slightly larger than the values found for the corresponding bond in the phenol–imine tautomers, the C1=C11 bond lengths are between Csp^2–Csp^2 in α,β-unsaturated carbonyls and Car–C=N– values (1.476(14) and 1.340(13) Å, respectively) [32]. Finally, C11=N1 bond lengths show values (1.310(5) and 1.303(3) Å, respectively) corresponding to conjugated C=N groups (1.279(8) Å) [32]. The short C3=C4 bonds, i.e. 1.339(5) and 1.347(4) Å, respectively, also confirm the quinonoid character of both compounds [7,10,13,33]. Furthermore, compound (**2**) shows the same features, and in the crystalline state, was also found as the keto–amine tautomer [7].

Although the molecules of (**1**), (**3**), (**5**), (**7**), (**8**) and (**9**) show strong intramolecular hydrogen bonds that "lock" planar their corresponding salicylaldimino or naphthaldimino moieties, due to the non-aromatic nature of the substituent at the imino nitrogen, the molecules as whole are not planar.

On the other hand, because of the lack of precise localization of the hydrogen atom bonded to oxygen or nitrogen atoms in other X-ray crystal structures of

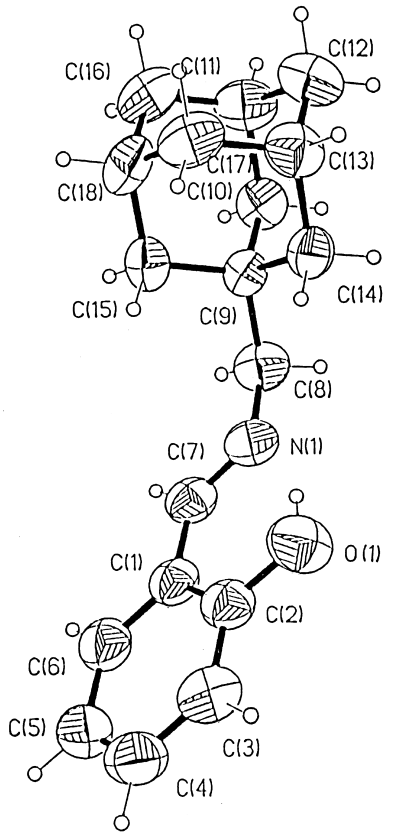

Fig. 4. Molecular structure of compound (**7**) in the solid state with the atom numbering scheme. Thermal ellipsoids are drawn at 50% of probability.

similar Schiff bases already reported [8,9] (the *n*-propyl- and *n*-butyl-1,2-naphthalenic analogs, respectively), it is difficult to determine whether, as they claimed, they actually synthesized, isolated and characterized the phenol–imine tautomers of those Schiff bases or maybe they misassigned their structures. However, they report unexpectedly short C2–O bond lengths (1.254(8) and 1.23(1) Å, respectively), and the C11–N bond length of the 1,2-Schiff base with *n*-propyl substituent is of the same order (1.313(8) Å) than the corresponding bond in (**5**) and (**8**) (the reported value for the *n*-butyl derivative is not very good, i.e. 1.31(2) Å).

3.2. NMR spectroscopy

The solution structures of (**1**)–(**9**), and the ^1H and ^{13}C NMR spectral assignments were confirmed by a

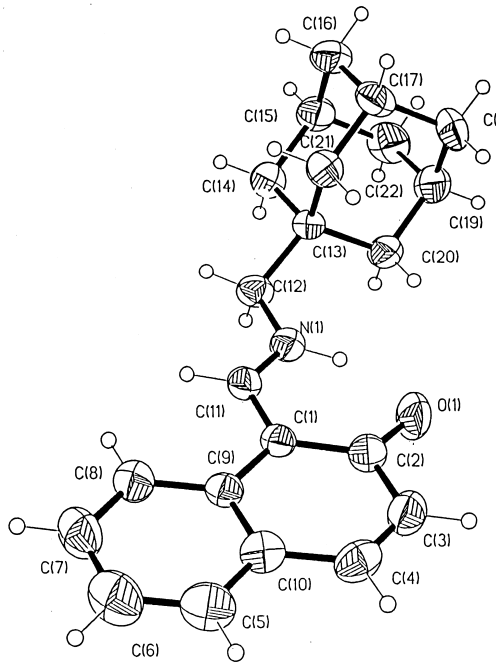

Fig. 5. Molecular structure of compound (**8**) in the solid state with the atom numbering scheme. Thermal ellipsoids are drawn at 50% of probability.

series of one-dimensional (^{1}H and ^{13}C, DEPT) and two-dimensional (COSY, HETCOR, FLOCK and NOESY) NMR experiments. The experiments were carried out in $CDCl_3$. Spectral assignments are summarized in Table 3. All assigned chemical shifts for the naphthalene and benzene rings are in agreement with similar compounds reported in literature [34,35]. For (**2**), (**5**) and (**8**), the crucial observation was provided by the chemical shift of the C2 atom (178.6, 177.1 and 178.0 ppm, respectively) and the scalar coupling constant magnitude between H11 and H–N is given as 12.5 Hz, which characterizes the keto–amine structure. The J_{HN-H11} measured at room temperature are very similar with those measured at 183 K. Coupling constants immersed in the linewidth of HN signals were measured by the *J* doubling method [36], which are in complete agreement with those measured in the H11 signals. Broad lines of HN signals are a consequence of the fast exchange rate of these protons [37]. Whereas, for compounds (**1**), (**3**), (**4**), (**6**), (**7**) and (**9**), the chemical shift of the corresponding C2 or C3 atoms are observed at higher fields (162.2, 157.3, 161.3, 157.0, 161.5 and 157.1 ppm, respectively), and there is absence of any H–HN coupling [35]. All data for both sets of compounds are in complete agreement with the X-ray structures and theoretical calculations.

Because under normal experimental conditions it was not possible to observe both tautomeric species for any compound, the ^{1}H and ^{13}C NMR spectra for compound (**8**) were obtained between 323 and 183 K in D6-acetone and D2-dichloromethane, to determine any possible isomers. However, no considerable changes were observed. This strongly suggests for this series of Schiff bases, that for all 1,2-naphthaldamines the keto–amine isomer form is the most stable, which is in good agreement with a low interchangeable activation energy between those isomers [38]. Meanwhile for the salicylaldamines and 2,3-naphthaldamines the

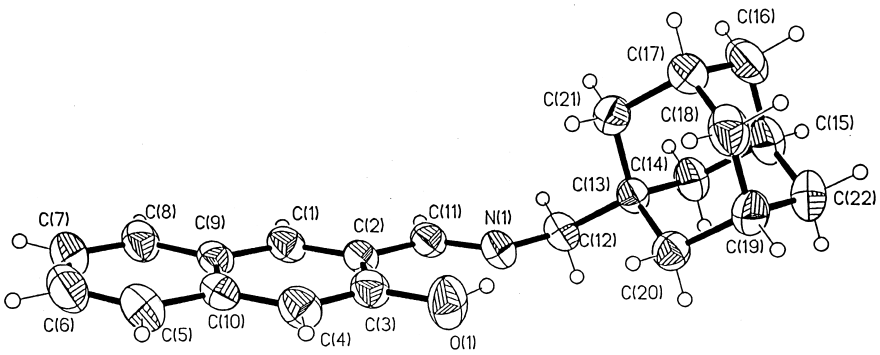

Fig. 6. Molecular structure of compound (**9**) in the solid state with the atom numbering scheme. Thermal ellipsoids are drawn at 50% of probability.

Table 3
Assigned ^{1}H and ^{13}C chemical shifts [in ppm relative to internal $Si(CH_3)_4$] for compounds (**1**)–(**9**)

	Compound																	
	(**1**)		(**2**)		(**3**)		(**4**)		(**5**)		(**6**)		(**7**)		(**8**)		(**9**)	
Carbon	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1	118.79	–	105.48	–	132.58	7.70(s)	118.67	–	105.85	–	132.45	7.63(s)	118.64	–	106.03	–	132.61	7.75(s)
2	162.22	–	178.62	–	121.44	–	161.27	–	177.11	–	121.29	–	161.55	–	177.97	–	121.16	–
3	117.26	6.91(dd)	125.93	6.86(d)	157.30	–	116.70	6.92(dd)	125.10	6.89(d)	157.03	–	116.92	6.94(dd)	125.56	6.90(d)	157.09	–
4	131.80	7.25(ddd)	137.09	7.59(d)	110.61	7.23(s)	131.62	7.23(ddd)	136.82	7.59(d)	110.65	7.24(s)	131.86	7.26(ddd)	137.31	7.65(d)	110.80	7.26(s)
5	117.81	6.81(ddd)	128.82	7.51(d)	126.03	7.63(dd)	117.96	6.80(ddd)	128.76	7.51(dd)	126.12	7.63(dd)	118.12	6.82(ddd)	129.13	7.57(dd)	126.24	7.67(dd)
6	131.16	7.21(dd)	121.90	7.14(dd)	127.59	7.39(m)	130.85	7.17(dd)	122.03	7.14(ddd)	127.75	7.39(ddd)	130.97	7.20(dd)	122.39	7.19(ddd)	127.90	7.44(m)
7	159.09	8.30(s)	127.47	7.36(dd)	122.95	7.23(m)	162.04	8.26(s)	127.47	7.34(ddd)	123.10	7.23(m)	164.72	8.20(s)	127.80	7.39(ddd)	123.26	7.27(m)
8	56.94	–	117.04	7.78(d)	128.15	7.70(dd)	66.97	3.14(m)	117.29	7.78(dd)	128.21	7.68(dd)	72.14	3.20(s)	117.44	7.80(dd)	128.27	7.74(m)
9	42.82	1.81(d)	134.02	–	127.13	–	33.97	1.62(m)	133.68	–	127.16	–	33.94	–	133.93	–	127.25	–
10	29.26	2.15(bs)	125.44	–	135.46	–	24.00	1.45(m)	125.56	–	135.59	–	40.67	1.54(s)	125.87	–	135.71	–
11	36.18	1.70(dd)	151.24	8.64(d)	159.05	8.42(s)	25.23	1.38(m)	154.97	8.68(d)	162.10	8.37(s)	28.28	1.96(dd)	157.86	8.53(d)	164.75	8.40(s)
12	29.26	2.15(bs)	54.33	–	57.53	–	24.00	1.45(m)	60.14	3.28(m)	67.74	3.18(m)	36.83	1.66(dd)	65.12	3.17(dd)	72.85	3.27(s)
13	36.18	1.70(dd)	42.55	1.90(s)	42.71	1.80(s)	33.97	1.62(m)	33.36	1.66(m)	34.09	1.65(m)	28.28	1.96(dd)	33.85	–	34.22	–
14	29.26	2.15(bs)	28.86	2.14(s)	29.23	2.14(s)	–	–	23.79	1.52(m)	24.19	1.55(m)	40.67	1.54(s)	40.03	1.55(s)	40.89	1.59(s)
15	42.82	1.81(d)	35.45	1.67(dd)	36.15	1.69(dd)	–	–	24.75	1.36(m)	25.39	1.44(m)	40.67	1.54(s)	28.06	1.98(s)	28.40	1.99(s)
16	42.82	1.81(d)	28.86	2.14(s)	29.23	2.14(s)	–	–	23.79	1.52(m)	24.19	1.55(m)	36.83	1.66(dd)	36.59	1.66(dd)	36.95	1.69(dd)
17	36.18	1.70(dd)	35.45	1.67(dd)	36.15	1.69(dd)	–	–	33.36	1.66(m)	34.09	1.65(m)	36.83	1.66(dd)	28.06	1.98(s)	28.40	1.99(s)
18	–	–	28.86	2.14(s)	29.23	2.14(s)	–	–	–	–	–	–	28.28	1.96(dd)	36.59	1.66(dd)	36.95	1.69(dd)
19	–	–	42.55	1.90(s)	42.71	1.80(s)	–	–	–	–	–	–	–	–	28.06	1.98(s)	28.40	1.99(s)
20	–	–	42.55	1.90(s)	42.71	1.80(s)	–	–	–	–	–	–	–	–	40.03	1.55(s)	40.89	1.59(s)
21	–	–	35.45	1.67(dd)	36.15	1.69(dd)	–	–	–	–	–	–	–	–	40.03	1.55(s)	40.89	1.59(s)
22	–	–	–	–	–	–	–	–	–	–	–	–	–	–	36.59	1.66(dd)	36.95	1.69(dd)
OH	–	14.43(b)	–	–	–	13.82(b)	–	13.73(b)	–	–	–	13.24(b)	–	13.84(b)	–	–	–	13.25(b)
NH	–	–	–	14.67(b)	–	–	–	–	–	14.52(b)	–	–	–	–	–	14.50(b)	–	–

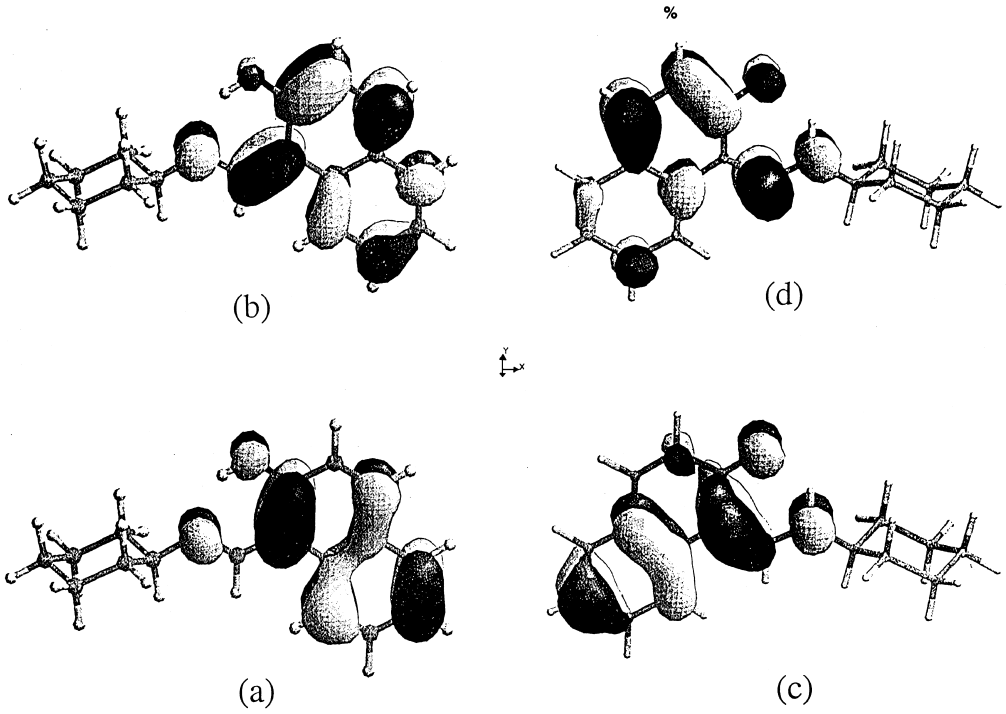

Fig. 7. Frontier orbitals, HOMO–LUMO, of: (a,b) phenol–imine and (c,d) keto–amine tautomers of compound (**5**).

phenol–imine isomer form is the preferred structure in deuterochloroform solution.

3.3. Ab initio calculations

Theoretical calculations show that in the case of compound (**1**), the keto–amine form has an energy $U = -2061816.691$ kJ/mol, very close to that of the phenol–imine form $U = -2061820.900$ kJ/mol. The value of ΔG for the equilibrium between the keto–amine and phenol–imine forms is -4.17 kJ/mol, which suggest that both isomers could be found in solution; however, in a deuterochloform solution only the phenol–imine isomer was observed, and in the solid state the X-ray study also shows that only the phenol–imine form was isolated.

A similar analysis was carried out for the 1,2-naphthalenic compound (**5**), where a cyclohexyl substiuent is bonded to the nitrogen of the imine group. The calculations show an energy $U = -2058798.918$ kJ/mol for the keto–amine form and $U = -2058800.451$ kJ/mol for the phenol–imine form. A small preference for the keto tautomer with a $\Delta G = 1.246$ kJ/mol was found, which is in agreement with the value obtained by NMR spectroscopy for the *p*-methylaniline Schiff base adduct of 2-hydroxy-1-naphthaldehyde [35]. Fig. 7 shows the frontier orbitals, HOMO–LUMO, of both keto–amine and phenol–imine tautomers of compound (**5**) resulting from the calculations.

Hence, all data analyzed here suggest that all the 2-hydroxy-1-naphthaldehyde Schiff base adducts of alkyl- or cycloalkylamines are always found in the solid state as well in solution as the keto–amine tautomer. Furthermore, the non-planarity of the compounds analyzed by X-ray crystallography suggest a photochromic behavior [5] in the crystalline state, nevertheless, this feature should to be demonstrated.

Supplementary material has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 26654.

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