Tautomerism in Schiff bases derived from 3-hydroxysalicylaldehyde. Combined X-ray diffraction, solution and solid state NMR study

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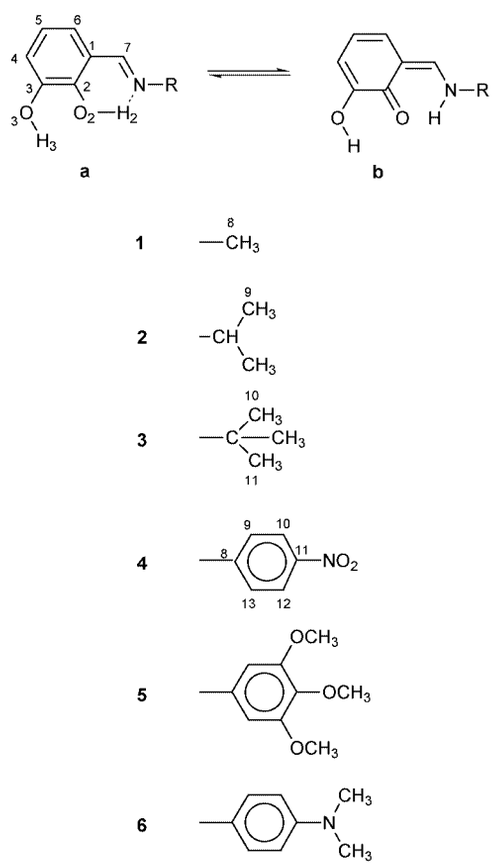
Received (in Cambridge, UK) 27th January 2000, Accepted 16th March 2000

The crystal structure of six Schiff bases derived from 3-hydroxysalicylaldehyde has been determined by single crystal X-ray diffraction. In the solid state, these compounds form dimers linked by two strong intermolecular O–H · · · O bridges resulting in ten-membered pseudocycles. From the observed geometrical parameters together with previous results obtained for *N*-(3-hydroxysalicylidene)isopropylamine, it can be concluded that these compounds undergo a fast proton exchange between two forms, phenol–imine and keto-amine. The tautomeric equilibrium mixture is greatly influenced by the physical state of the examined compounds. This is clearly seen when comparing results obtained from liquid and solid-state ^{13}C NMR. For derivatives derived from aliphatic amines the keto-amine tautomer is always predominant; for compounds obtained from substituted anilines the tautomeric concentration is variable depending on the nature of the substituent. An excellent correlation between C–O bond lengths and ^{13}C chemical shifts is observed.

Introduction

The photochromic and thermochromic behaviour of *N*-salicylideneamines and particularly the effect on these properties of substitutions and/or chemical modifications of the molecules has been the subject of many studies.[1] The overall behaviour of these compounds has been ascribed to a proton transfer reaction between a phenol–imine and a keto-amine tautomer. The possibility of stabilizing the keto-amine form to strengthen the thermochromic character of these derivatives has been for some time a preoccupation of our laboratory.[2] We found that this shift towards the keto-amine form could not be achieved very efficiently through a simple modification of the nature of the R groups. This led us to focus on the salicylidene moieties modified by introducing another hydroxyl group in *ortho* position to the original one. An equilibrium reaction such as that shown in Scheme 1 is expected for these *N*-(3-hydroxysalicylidene)amine compounds. Owing to the electron donating character of the added OH group and its effect on proton release, one can predict a decreased acidity for the other OH group. This should lead to less proton transfer from the hydroxyl oxygen to the azomethine nitrogen. Moreover this substituent will participate in intra- and/or inter-molecular hydrogen bonds likely to influence the proton transfer process. In solution however IR and electronic absorption studies demonstrated that the effect of this substituent is in fact very small. The amount of keto-amine is not at all enhanced.[3] This is no longer the case when the compounds are in the solid state. Structural results have indeed shown[3–5] that for certain compounds of a *N*-(3-hydroxysalicylidene)amine series (with R = alkyl or aryl) the quinoid tautomer becomes the dominant species. In this case, the increase of hydrogen transfer from oxygen to nitrogen has been ascribed[3] to the presence of an intermolecular hydrogen bond O(3)–H(3) · · · O(2). In the crystalline lattice these molecules are present mainly as dimers but trimers or even polymeric associations are also formed.[3,4] These compounds are exclusively thermochromic because their compact structure inhibits the intramolecular isomerization required to exhibit photochromic properties. In this work our main concern is to evaluate the importance of proton transfers occurring in six thermochromic



Scheme 1 Tautomeric equilibrium in compounds **1**–**6**.

DOI: 10.1039/b000756k

compounds (**1**–**6** see Scheme 1) using both X-ray diffraction and ^{1}H, ^{13}C NMR spectroscopy. So far, the dynamics of this problem had only been studied by IR.[3,6] Two series of compounds were synthesized (Scheme 1): one (**1**–**3**) with aliphatic R groups (R = Me, iPr, tBu), the other formed of phenyl derivatives bearing different substituents (**4**–**6**). The substituents were chosen for their well-known electron-donating or electron-withdrawing properties.

Experimental

All compounds were synthesized by standard procedures by condensation of 2,3-dihydroxybenzaldehyde with the appropriate amine. Suitable crystals for X-ray analysis were obtained by slow evaporation of the solvent from a concentrated ethanolic solution.

Crystal structure determination of compounds 1, 4, 6

X-Ray data were collected at room temperature on a Nonius Kappa CCD diffractometer with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using phi scan mode. Crystal data of **1**, **4**, **6** as well as details about data collection and refinements are summarized in Table 1. Structures were solved and refined by using the MAXUS program.[7] Selected bond distances and angles are listed in Table 2 and Table 3, respectively.

CCDC reference number 188/235.

See http://www.rsc.org/suppdata/p2/b0/b000756k/ for crystallographic files in .cif format.

NMR measurements

^{1}H and ^{13}C solution measurements were performed on a Bruker AMX 400 NMR spectrometer operating at 400.13 and 100.62 MHz, respectively. Spectra were collected in $CDCl_3$ or CCl_4. In the latter case the resonances were referenced with an external capillary of C_3D_6O and then converted into the TMS scale. Solid state ^{13}C CPMAS NMR spectra were recorded at 75.5 MHz on a Bruker DSX 300 spectrometer. About 200 mg of polycrystalline powder sample were packed in a 4 mm zirconium rotor and spun at about 6 kHz. Spectral conditions were as follows: spectral width, 30 kHz; proton 90° pulse, 3.8 μs; recycle delay, 5–100 s; number of acquisitions 100–1000; cross polarization time, 10–20 ms, and 10–20 μs in short contact time experiments. The long cross polarization time was optimized for these compounds in order to obtain the best intensity ratios between quaternary and protonated carbons. It should be noted that the loss of polarization of the CH carbons for these long contact times is very small. For the short contact time experiments the chosen cross polarization time is much smaller than 200 μs, the classical value normally used; these short values were necessary to remove from our spectra certain quaternary carbons still present for longer contact times. The dipolar dephasing sequence with a refocusing π pulse was applied using a 40 μs dephasing window for the selective removal of signals from rigid protonated carbons. Nitrogen gas was used as bearing and driving gas during the low temperature measurements. Temperatures were measured with a thermocouple placed in the cooling gas stream. Temperature uncertainties are estimated to be no more than 10 °C. Calibration of the ^{13}C CPMAS spectra was done by replacing the sample by a TMS filled rotor. This procedure was carried out before each new experimental run.

Results and discussion

X-Ray diffraction analysis

For all compounds, the salicylidene ring bond lengths were found to follow the alternating sequence: C(1)–C(2) < C(2)–C(3) > C(3)–C(4) < C(4)–C(5) > C(5)–C(6) < C(6)–C(1). This observation could result from a resonance form of the phenol–imine tautomer or equally well from a contribution of the quinoid species. The gap between the shortest bonds of C(3)–C(4) and C(5)–C(6) located in the range 1.34 to 1.39 Å and all others found between 1.40 and 1.43 Å is large. Except for compound **6**, all C(2)–O(2) distances are much shorter than 1.37 Å which is the characteristic value for phenolic structures and observed for all compounds in the case of C(3)–O(3). The shortest C(2)–O(2) bond length, 1.289(7) Å, is found in compound **3a**; this value corresponds to the one expected for a quinoid structure.[8] For all compounds, the salicylidene group is characterized by short O(2)···N distances (Table 4) much shorter than the sum of the van der Waals radii for nitrogen and oxygen.[9] This is indicative of a strong intramolecular hydrogen bond leading to planar salicylideneimine moieties. The O(2)···O(3) values listed in Table 4 suggest the presence of an additional weaker intramolecular hydrogen bond. R groups containing substituted aromatic rings have C–C bond lengths close to 1.39 Å which is the value found in benzene. Bond angles are around 120° except C(8)–N–C(7) which has a higher value probably due to a steric interaction between H(7) and H(10) so no correlation with the C(2)–O(2) distance can be made. Dihedral angles between the salicylidene planes and the substituted aromatic fragments are small and do not exceed 5 degrees. These molecules can therefore be considered as planar as found for most thermochromic crystalline *N*-salicylideneamine derivatives.[8d,10] Except for two[4] all other compounds are composed of dimers forming ten-membered pseudocycles O(2)–C(2)–C(3)–O(3)–H(3)^{I}···O(2)–C(2)–C(3)–O(3)–H(3)^{II}···O(2)^{I} characterized and stabilized by two intermolecular and two intramolecular interactions. The two intermolecular hydrogen bonds O(3)–H(3)···O(2) are indeed characterized by relatively short O(2)^{I}···O(3)^{II} and O(3)^{I}···O(2)^{II} distances (shorter than the sum of van der Waal radii of oxygen atoms, 3.04 Å[9]) (see Table 4). The observed distances are of the order of the ones found in carboxylic acid dimers[11] which are planar contrary to the pseudocycles formed in our case. The dimers of compounds **2**, **4**, **5** and **6** have a symmetry center with all molecules lying in parallel planes separated by a mean distance of 0.4 to 1.5 Å. For compounds **1** and **3** the asymmetric unit is characterized by two independent molecules not associated as dimers with a symmetry center (as illustrated in Fig. 1). The angles between the mean planes of the two salicylidene units are respectively 61.5° for sample **1** and 74.0° for sample **3**. The crystal packing resulting from a dimer association is highly compact. Distances between planes of non-associated molecules are smaller than 3.5 Å which prevents intermolecular rotation and consequently photochromism. The O(3)–H(3)

Table 1 Crystal data and data collections of compounds **1**, **4**, and **6**

	1	**4**	**6**
Formula	$C_{16}H_{18}N_2O_4$	$C_{13}H_{10}N_2O_4$	$C_{15}H_{16}N_2O_2$
M	302.24	258.53	256.30
Crystal system	Triclinic	Triclinic	Monoclinic
a/Å	6.855(1)	7.005(1)	10.246(1)
b/Å	7.551(1)	7.180(1)	6.106(1)
c/Å	14.622(1)	12.018(1)	20.863(1)
α/°	80.66(1)	83.21(1)	90.00(1)
β/°	88.46(1)	79.16(1)	90.42(1)
γ/°	87.17(1)	72.66(1)	90.00(1)
V/Å^3	746.0(1)	565.0(2)	1305.2(3)
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Z	2	2	4
μ/mm^{-1} (Mo-K$_\alpha$)	0.098	0.115	0.088
No. of reflections			
measured	5420	3628	8926
unique	2795	1968	2628
observed data	2166	1039	1391
wR	0.063	0.150	0.068
R	0.042	0.074	0.048
R_{int}	0.060	0.035	0.041

Table 2 Distances (Å) observed for compounds **1**–**6**[a] with estimated standard deviation (esds) in parentheses

	1a	1b	2[4]	3a[5]	3b[5]	4	5[5]	6
C1–C2	1.426(1)	1.422(1)	1.433(3)	1.422(8)	1.416(8)	1.421(2)	1.422(4)	1.403(1)
C2–C3	1.427(1)	1.429(1)	1.430(3)	1.417(8)	1.409(8)	1.428(2)	1.423(4)	1.400(1)
C3–C4	1.361(1)	1.365(1)	1.370(3)	1.352(8)	1.409(8)	1.383(2)	1.350(4)	1.374(1)
C4–C5	1.409(1)	1.405(1)	1.409(3)	1.410(8)	1.380(8)	1.401(2)	1.409(4)	1.397(1)
C5–C6	1.357(1)	1.368(1)	1.355(2)	1.340(10)	1.380(10)	1.359(2)	1.354(4)	1.373(1)
C6–C1	1.420(1)	1.419(1)	1.425(3)	1.411(9)	1.410(9)	1.434(2)	1.410(4)	1.397(1)
C2–O2	1.295(1)	1.299(1)	1.294(3)	1.289(7)	1.308(7)	1.317(2)	1.304(4)	1.336(1)
C3–O3	1.359(1)	1.364(1)	1.372(2)	1.363(7)	1.365(8)	1.364(2)	1.365(3)	1.368(1)
C1–C7	1.414(1)	1.423(1)	1.412(3)	1.430(8)	1.427(8)	1.407(2)	1.424(4)	1.438(1)
C7–N	1.302(1)	1.299(1)	1.301(3)	1.287(8)	1.285(8)	1.325(2)	1.292(3)	1.290(1)
N-C8	1.456(1)	1.467(1)	1.470(3)	1.462(8)	1.460(8)	1.424(2)	1.410(3)	1.418(1)
C8–C9			1.500(4)	1.520(20)	1.490(10)	1.389(2)	1.387(4)	1.374(1)
C8–C10			1.515(4)	1.520(20)	1.480(10)			
C8–C11				1.470(10)	1.490(10)			
C9–C10						1.389(2)	1.381(3)	1.379(1)
C10–C11						1.384(2)	1.396(4)	1.389(1)
C11–C12						1.367(2)	1.394(4)	1.394(1)
C12–C13						1.400(2)	1.381(4)	1.387(1)
C13–C8						1.409(2)	1.389(1)	1.379(1)

[a] Structural formula are given in Scheme 1.

Table 3 Selected bond angles (°) of different compounds[a] with esds in parentheses

	1a	1b	2[4]	3a[5]	3b[5]	4	5[5]	6
C6–C1–C2	120.5(1)	120.9(1)	120.2(2)	120.6(5)	120.6(5)	120.2(2)	119.6(2)	119.9(1)
C7–C1–C2	120.2(1)	119.9(1)	119.2(2)	118.9(6)	120.4(6)	120.4(2)	118.6(2)	120.2(1)
C7–C1–C6	119.4(1)	119.2(1)	120.5(2)	120.4(5)	119.0(5)	119.4(2)	121.8(2)	119.8(1)
C3–C2–C1	116.6(1)	116.6(1)	116.6(2)	116.5(5)	117.6(5)	117.7(2)	118.0(2)	119.2(1)
O2–C2–C1	122.7(1)	123.0(1)	123.0(2)	122.9(5)	121.9(5)	122.6(2)	122.8(2)	122.4(1)
O2–C2–C3	120.7(1)	120.5(1)	120.4(2)	120.7(6)	120.5(5)	119.7(2)	119.3(2)	118.4(1)
C4–C3–C2	121.5(1)	121.4(1)	121.4(2)	121.8(6)	121.4(6)	120.3(2)	120.6(2)	120.1(1)
O3–C3–C2	119.3(1)	118.7(1)	118.6(2)	117.9(5)	118.8(5)	118.7(2)	117.8(2)	120.7(1)
O3–C3–C4	119.2(1)	119.9(1)	120.1(2)	120.4(6)	119.7(6)	121.0(2)	121.5(2)	119.2(1)
C5–C4–C3	121.0(1)	121.2(1)	121.0(2)	120.6(6)	120.0(6)	121.3(3)	121.0(3)	120.6(1)
C6–C5–C4	119.5(1)	119.7(1)	120.0(2)	120.1(7)	121.7(6)	120.3(2)	120.2(3)	120.0(1)
C5–C6–C1	120.5(1)	120.2(1)	120.7(2)	120.4(7)	118.7(6)	120.2(2)	120.6(3)	120.2(1)
N-C7–C1	122.4(1)	122.4(1)	124.1(2)	123.0(6)	121.6(6)	121.3(2)	121.6(2)	121.0(1)
C8–N-C7	123.8(1)	124.2(1)	125.2(2)	128.3(5)	127.8(5)	125.6(2)	129.6(2)	124.0(1)

[a] Structural formula are given in Scheme 1.

Table 4 Characteristic distances (Å) of intra- and inter-molecular hydrogen bonds

	1a	1b	2[4]	3a[5]	3b[5]	4	5[5]	6
Intramolecular								
O2 ··· N	2.578(1)	2.584(1)	2.596(5)	2.565(5)	2.558(8)	2.555(2)	2.505(3)	2.549(1)
O2 ··· O3	2.752(1)	2.739(1)	2.742(2)	2.713(6)	2.732(6)	2.735(2)	2.698(3)	2.733(1)
Intermolecular								
$O2^{I} \cdots O3^{II}$		2.709(1)[a]	2.699(3)	2.711(7)[b]	2.738(7)[c]	2.730(2)	2.746(3)	2.800(1)
$O2^{II} \cdots O3^{I}$		2.669(1)		2.554(7)	2.711(7)			
$O2^{I} \cdots O2^{II}$		3.198(1)	3.194(3)	3.008(7)	3.128(7)	3.243(2)	3.098(3)	3.323(1)
$O3^{I} \cdots O3^{II}$		3.771(1)	4.406(3)	3.801(7)	3.801(7)	4.400(2)	4.475(3)	4.425(1)

[a] I: a(x, y, z) II: b(x, y, z). [b] I: a(x, y, z) II: b($-\frac{1}{2} + x$, y, $-\frac{1}{2} - z$). [c] I: b(x, y, z) II: a($\frac{1}{2} + x$, y, $-\frac{1}{2} - z$).

groups present in our compounds form strong intermolecular interactions as shown by the shortening of the C(2)–O(2) distances. A detailed infrared spectroscopy study of compounds **2**,[3] **3** and **5**[5] showed that both keto-amine and phenol–imine tautomers are present in the crystalline state. Therefore, measured bond lengths of the two molecular structures in equilibrium correspond to weighted averages. Assuming for C(2)–O(2) a value of 1.251 Å for a pure quinoid species (as estimated by semi-empirical MO AM1 calculations[12] and measured as 1.254(8) Å for *N*-*n*-propyl-2-hydroxy-1-naphthaldimine[13]), our results suggest, except for compound **6**, the presence of a dominant keto-amine tautomer. In Schiff bases derived from salicylaldehyde a similar value of 1.257(2) Å was observed for *N*-(5-nitrosalicylidene)ethylamine.[14] However, in this compound, the phenol acidity is increased by a co-operative *para* and *ortho* through-resonance effect which is not present in our aliphatic compounds. This explains why our observed values are in the range 1.289(7) to 1.308(7) Å, *i.e.* higher than 1.257(2) Å. In the case of substituted aromatic R fragments, the C(2)–O(2) bond lengths are larger than those previously reported but shorter than the distance found for aniline derivatives (1.344(4) Å).[4] For compounds **4** and **5** the measured values are respectively 1.317(2) and 1.304(4) Å which are close to the estimated 1.305 Å for the pure quinoid structure of *N*-(5-chlorosalicylidene)-4-hydroxyaniline[15] but larger than 1.279(4) Å in the case of *N*-(3-hydroxysalicylidene)-2-hydroxymethylaniline.[16] We can there-

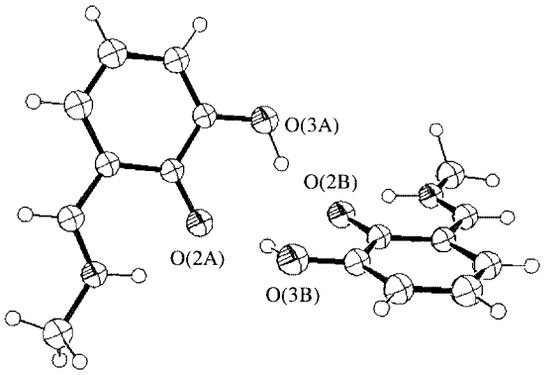


Fig. 1 Non-centrosymmetric dimeric association in compound **1**.

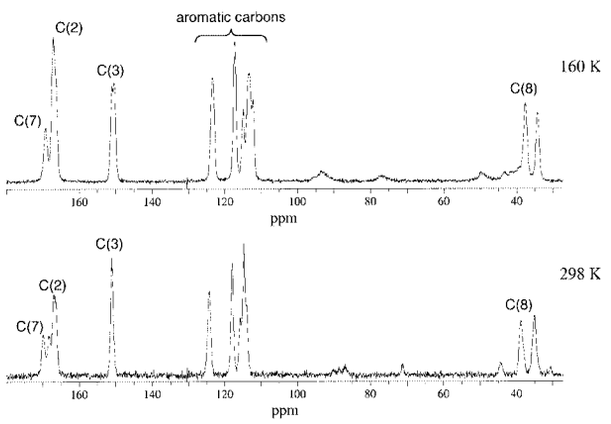


Fig. 2 ^{13}C CPMAS spectra of compound **1** (two molecules in the asymmetric unit).

fore assume that compounds **4** and **5** are essentially quinoid with a small amount of phenolic tautomer present in compound **5**.

High resolution NMR study

Solution. In $CDCl_3$ certain ^1H lines exhibit a pronounced down-field resonance with shifts between 12.7 and 14.5 ppm characteristic of acidic protons involved in strong intramolecular hydrogen bonds such as H(2). Higher chemical shifts were observed for Schiff bases derived from 2-hydroxynaphthaldehyde and 3,4,5,6-tetrachlorosalicylaldehyde.[17] The signal due to H(3) is very broad whatever the concentration and is observed systematically in the range 5.7–6.2 ppm. These lower values of chemical shifts indicate that H(3) is less acidic than H(2) and involved in weaker intramolecular hydrogen bonds.

As the chemical shift of carbon is sensitive to the presence of bound nitrogen or oxygen, we also ran ^{13}C NMR spectra in CCl_4 (an apolar and aprotic solvent) to obtain the specific carbon chemical shifts of the pure and isolated phenol–imine tautomer. The experimental ^{13}C chemical shifts are given in Table 5. The values are clearly sensitive to the tautomeric equilibrium position and to the physical state of the compound. In solution, *N*-(3-hydroxysalicylidene)amines display a pure phenolic character whatever the nature of the R fragment (aliphatic or aromatic) as is the case for *N*-salicylideneamine.[18,19]

Solid state. Chemical shift assignment was facilitated by taking into account the crystallographic specificities of each compound and running the spectra with short contact times and/or dipolar dephasing. Significant chemical shifts are summarized in Table 5. The ^{13}C NMR spectra of our solid *N*-(3-hydroxysalicylidene)amine derivatives will be interpreted as reflecting the presence of a rapid **a** to **b** equilibrium mixture (see Scheme 1). From a comparison of the solution-solid spectra (Table 5), it is observed for the solids: (i) an increase of the δ C(2) values; (ii) an overall decrease for δ C(7), δ C(8) and δ C(1). These variations are indicative of a shift of the tautomeric equilibrium towards the keto-amine form.[18,20] For the aliphatic derivatives the increase of δ C(2) towards higher values is significant. The resonance of carbons C(7) and C(8) strongly depends on the nature of the R fragments and differs from the values found for the aromatic compounds. The values for C(7) are consistent with those observed for enamines bearing aliphatic substituents.[14] These results therefore clearly show that for all solid compounds a definite increase (to various degrees) of the quinoid character is observed. For a fast tautomeric exchange process, the observed chemical shift $\langle\delta\rangle$ is given by $\langle\delta\rangle = x_a\delta_a + x_b\delta_b$ with $x_a + x_b = 1$, which is an average of the chemical shifts of the isolated tautomers (δ_a and δ_b) weighted by their respective contributions x_a and x_b. The value of $\langle\delta\rangle$ can be used to extract information on the position of the tautomeric equilibrium.[18,20,21] A standard procedure for studying exchange processes is to try and isolate exchanging species by running low temperature NMR experiments. The success of such an undertaking depends on the rate at which the exchange proceeds and therefore on the temperature which experimentally can be obtained. Many problems have been solved by NMR using the commonly available temperature range which in the case of MAS is limited to the 160–120 K region.[22–24] Therefore in order to try and freeze out the dynamic process and isolate each tautomer, variable temperature CPMAS experiments were run between 298 and 140 K on three selected derivatives, **1**, **2** and **5**. For compounds **1** and **5** no shift or broadening of the lines is observed when the temperature is lowered to respectively 140 and 170 K. For compound **1**, however, a decrease in temperature to 160 K induces some small changes in the ^{13}C CPMAS spectrum (*cf.* Fig. 2): (i) an overlapping induced by a slight shift of the C(7) signal towards the C(2) lines; (ii) a 0.5 ppm splitting of the C(3) line and (iii) a slight modification of lines in the 110 to 120 ppm range containing the C(1) resonance. However, the C(8) lines remain unchanged. In the temperature range which we could cover the observed spectral modifications are therefore not indicative of a change in the tautomeric equilibrium which should mainly affect the C(2), C(7), C(8) and C(1) lines. This conclusion is supported by X-ray diffraction measurements at 170 K which show no major molecular modifications.[25] These results suggest two possible situations: (i) the existence of a single resonance structure; (ii) a high rate dynamic exchange between tautomer **a** and **b** with a low activation barrier. Previous IR results[3,6] carried out on these solids had confirmed the presence of a dynamic process involving both tautomers. In the case of salicylideneaniline derivatives Takeda *et al.*[26] estimated the activation energy of such a process to be around 2 kJ mol^{-1}. In our case the NMR experiments should be extended to a much lower temperature region as recently done by Benedict *et al.* (to 26 K)[27] by use of a cryogenic CPMAS probe. Consequently, only a qualitative estimation of the respective contribution of each tautomer (**a** and **b**) can be given here. For that purpose, an estimation of the characteristic C(2) chemical shift of each species is needed. For the phenol–imine form the value 161 ppm observed for salicylideneamines[18,28] cannot be used here owing to the electron-donating influence of the second OH group. For this substituent a shielding effect of about −12 ppm can be assumed as the observed chemical shift values found in solution are around 149 ppm. For the quinoid tautomer of salicylideneamines the δ C(2) value is estimated to be about 180 ppm.[18] This value should then be corrected by −12 ppm to give an approximate value for the pure quinoid of 168 ppm. With these assumptions a keto-amine tautomer of over 80% is found for all samples except compound **6** (26%). These results are in good agreement with the C(2)–O(2) bond lengths analysis discussed above. The shortest distances found for the aliphatic compounds are really representative of a highly dominating keto-

Table 5 ^{13}C chemical shifts (ppm) in solution and solid state

Compound		C1	C2	C3	C7	C8
1	Solution	115.84	149.22	145.27	165.94	45.28
	Solid[a]	114.2	166.5, 166.0	151.0	168.3, 169.9	35.1, 38.8
2	Solution	117.09	150.39	145.38	161.77	59.00
	Solid	114.5	167.5	150.5	165.2	55.1
3	Solution	116.18	153.04	146.18	159.07	55.99
	Solid[a]	112.1	166.9	150.5	162.1, 164.7	55.6, 56.3
4	Solution	118.17	148.51	145.34	165.21	153.73
	Solid	115.2	165.7	146.9	156.1	147
5	Solution	118.17	148.34	145.19	161.04	143.41
	Solid	114.6	163.0	148.6	152.3	132.4
6	Solution	118.63	148.57	145.46	160.24	141.83
	Solid	117.9	154.0	145.9	154.0	132.0

[a] Asymmetric unit constituted of two independent molecules.

amine form. In the solid state the contribution of the quinoid structure is strongly dependent on the nature of R (either aliphatic or aromatic). All compounds derived from *para* substituted anilines seem to give at first sight unexpected results difficult to explain in a simple manner. Indeed, despite a similar hydrogen-bonded dimeric association, the electron-withdrawing substituents (*p*-nitro) favour the stabilization of the quinoid structure whereas the *N*,*N*-dimethylamino groups stabilize the phenol–imine tautomer. This illustrates the well known fact that in the solid state the proton transfer processes are complex and differ from the ones proposed for isolated molecules.[29]

Conclusion

This study of six *ortho*-hydroxylated *N*-salicylideneamines has shown that in the crystalline state all compounds are associated as dimers (with or without a symmetry center) thus allowing the formation of ten-membered pseudocycles. Using previous results obtained by IR together with considerations concerning the variation of C–C bond lengths and C(2)–O(2) distances, it is shown that the molecular structure of these compounds can be described by a model wherein the phenol–imine and keto-amine tautomers are in fast exchange. The compounds derived from aliphatic amines are characterized by a dominant keto-amine tautomer. For compounds with an aryl fragment R, the position and nature of R may favour one form or the other; however the proportion of quinoid species is always significant. This effect had not yet been observed in the case of *N*-salicylideneanilines. As expected these observations concerning the solid-state tautomeric equilibrium do not necessarily correlate with the known elementary electronic substituent effects operating in the case of isolated molecules. The correlation between results obtained by X-ray diffraction and solid state NMR are found here to be very good.

Acknowledgements

We would like to thank the Structural Bio-Inorganic Departement of Marseille where the X-ray diffraction experiments were run. We are grateful to Dr F. Lefebvre for his assistance in obtaining the high resolution solid-state NMR spectra.

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