^{13}C NMR Spectroscopic and AM1 Study of the Intramolecular Proton Transfer in Anils of Salicylaldehyde and 2-Hydroxynaphthalene-1-carbaldehyde

Sergio H. Alarcón,[a] **Alejandro C. Olivieri** *[,a] **and Manuel González-Sierra**[b]
[a] *Departamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Suipacha 531, Rosario (2000) Argentina*
[b] *IQUIOS, Facultad de Ciencias Bioquímicas y Farmacéuticas, Suipacha 531, Rosario (2000) Argentina*

Tautomeric equilibria in intramolecularly hydrogen bonded Schiff bases is studied on the basis of solution ^{13}C NMR chemical shifts. Variable temperature NMR spectroscopic data and comparison with appropriate models show that while anils of salicaldehyde exist as phenolic tautomers, those of 2-hydroxynaphthalene-1-carbaldehyde exist as equilibrium mixtures containing appreciable amounts of both enol and keto tautomers, the latter being slightly predominant. AM1 results concerning the relative stability of tautomers are in good agreement with the NMR spectroscopic information.

Intramolecular proton transfer reactions have attracted considerable attention, both from experimental and theoretical points of view.[1,2] Recently, the possibility that these type of processes also occur in solid materials has been confirmed for a variety of compounds.[3] This has added a new vista to the relatively old subject of proton motion along strong hydrogen bonds. Several cases of hydrogen exchange between O · · · O, N · · · N and also N · · · O atoms have been reported.[3] Pertinent examples of the latter are arylazonaphthols displaying the equilibrium **a** $\rightleftharpoons$ **b** (Scheme 1).[4,5] Unlike arylazophenols, which mainly exist as **c** tautomers (Scheme 1),[5] arylazonaphthols have been shown to contain significant amounts of both **a** and **b** forms in equilibrium in both phases.[6] Furthermore, a significant shift in the tautomeric equilibrium **a** $\rightleftharpoons$ **b** has been detected in both phases upon changing the substituent R.[4,7] Molecular systems which also show the potential of a similar intramolecular reaction are the anils **1–10**.[8–10] Compounds such as **1–5** and related structures are known to exist mainly in the phenolic form **e** both in solution[10] and in the solid state,[8,9] as is the case with arylazophenols. As could be anticipated on a rather intuitive basis, Schiff bases **6–10** could also have appreciable amounts of the quinonoid tautomer **h** in equilibrium with the phenolic form **g**.

Intramolecularly hydrogen bonded Schiff bases have attracted attention as crystals of some of these compounds exhibit thermochromism and photochromism.[8,9,11] Thermochromism is known to involve an intramolecular proton shift to the quinonoid tautomer; this shift occurs both in the ground state and in the excited state. Photochromism involves a proton migration in the excited state, apparently coupled to a double bond isomerization, although the exact nature of the photoproducts is still a matter of some debate. Excited-state proton transfer (ESIPT) in solids also deserves attention as it is related to the photoprotection of polymers.[12]

In the present work, we report a ^{13}C NMR spectroscopic study of the tautomeric equilibrium in several anils derived both from salicaldehyde and from 2-hydroxynaphthalene-1-carbaldehyde. Chemical shifts have been measured in solution, and equilibrium compositions have been estimated from the consideration of suitable model compounds. Variable temperature measurements on compounds **3** and **8** lend additional support to the proton transfer tautomeric model, and allows thermodynamic information on the tautomeric equilibrium to be obtained. Minor changes in the equilibrium compositions with the nature of the R group are detected, and attempts to explain this result on a theoretical basis have been made by use of the semi-empirical MO program AM1. A comparison is made with similarly substituted arylazonaphthols.

Experimental

All compounds studied were prepared by standard procedures.

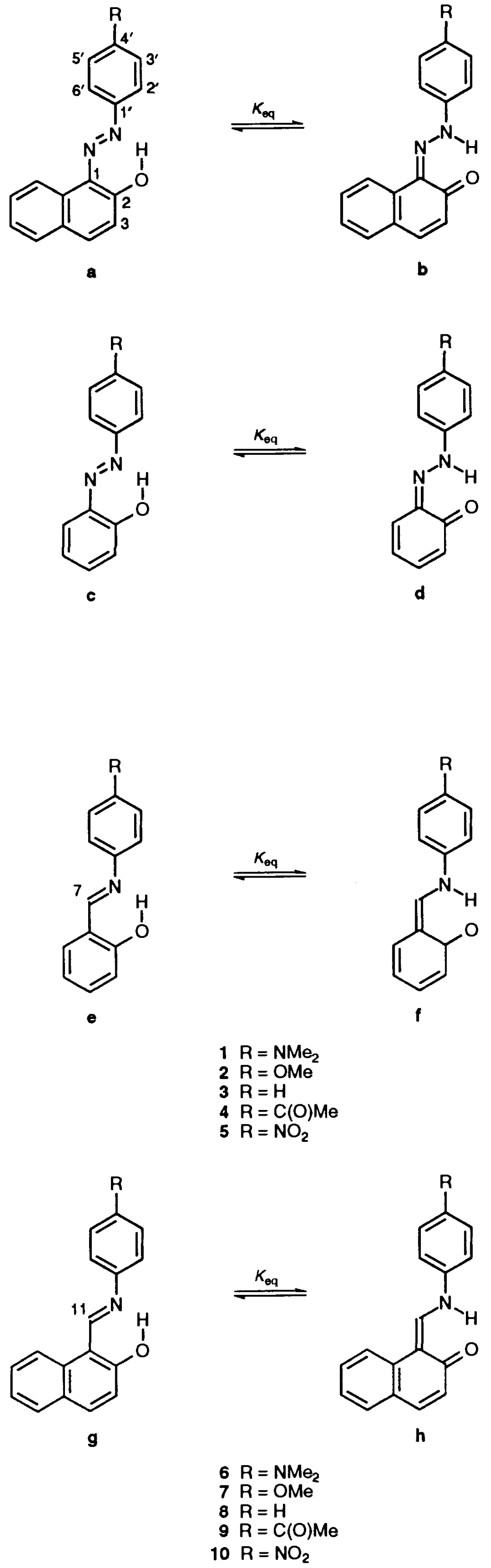
Solution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 NMR spectrometer operating at nominal frequencies of 200.1 and 50.3 MHz respectively. All chemical shifts were referenced against tetramethylsilane. Low temperature measurements were performed by cooling the sample with evaporated liquid N_2. Temperatures were measured with a previously calibrated thermocouple, and are considered accurate within ± 1 K.

AM1 calculations were performed by using the AMPAC package, version 2.10 with gradient optimization. In all cases the PRECISE option was used.

Results and Discussion

Satisfactory ^{1}H NMR spectra were obtained for all compounds studied. Anils **1–10** are characterized by an intramolecularly hydrogen bonded labile proton appearing at 12–13 ppm. Spectra are complicated by severely overlapped aromatic CH protons which proved to be rather uninformative as regards the tautomeric equilibrium under investigation.

As has been previously shown, the position of a tautomeric change such as **a** $\rightleftharpoons$ **b** (Scheme 1) can be conveniently monitored by ^{13}C NMR chemical shifts.[4,7] Carbons C-2 and C-1′–C-6′ have previously been shown to be sensitive to this type of equilibrium.[4,7] In the compounds presently studied, where R substituents affect the chemical shifts of the aromatic carbons C-1′–C-6′, the carbon of choice to study changes in equilibrium compositions is the C–O carbon C-2. Nevertheless, qualitative information in this regard can also be drawn from carbons C-1, C-4 and C-1′. In the case of arylazonaphthols, extreme values for C-2 have been estimated as *ca.* 147 ppm in **a** and 180 ppm in **b**.[4] In arylazophenols which are known to exist in the phenolic tautomer **c**, C-2 appears at about 153 ppm, indicating that a shielding of *ca.* 6 ppm occurs at C-2 in going from the phenol to the naphthol counterpart. Consideration of the relative substituent chemical shift (SCS) effects of –N=N- and –CH=N-groups[13] leads to the prediction that carbon C-2 will be relatively deshielded by the latter group. Since C-2 in tautomers of type **e** in salicylidene anilines appear at *ca.* 161 ppm (see below), it follows that the above mentioned



Scheme 1

deshielding amounts to about 8 ppm. Hence the extreme value for tautomer **g** in anils of 2-hydroxynaphthalene-1-carbaldehyde will be 155 ppm. In the absence of appropriate models for the quinonoid forms **f** and **h**, we assume a chemical shift for carbon C-2 in these tautomers of *ca.* 180 ppm. This argument allows the estimation, at least approximately, of the equilibrium constants for the intramolecular tautomerization reaction, by virtue of:

$$K_{eq} = (\delta - \delta_g)/(\delta_h - \delta) \qquad (1)$$

where δ is the chemical shift of the equilibrium-sensitive carbon C-2, δ_g is the extreme chemical shift assigned to carbon C-2 in tautomer **g**, and δ_h is that corresponding to tautomer **h**. It should be noticed that application of eqn. (1) to a series of compounds where the electronic nature of the substituent R is changed requires the intrinsic effect of R be known in order to correct the extreme chemical shifts δ_g and δ_h.[3d] Consideration of published ^{13}C NMR information for *p*-substituted benzylidene anilines shows that (besides the expected effect on C-1′–C-6′) *p*-substituents affect mainly the chemical shift of carbon C-7 (C-11 in **6–10**): R = NO_2, +2.4 ppm; R = MeO, −2.1 ppm.[14] Corresponding SCS effects on carbon C-2 are negligible.

Eqn. (1) has been previously applied to the case of arylazonaphthols,[4] and a significant shift in the tautomeric equilibrium was noticed towards the keto/hydrazo tautomer when the electron-withdrawing ability of R increases, both in solution and in the solid state.

Table 1 shows the observed ^{13}C NMR chemical shifts for the presently studied anils in $CDCl_3$ solution. In the case of those derived from salicaldehyde, **1–5**, C-2 shows the chemical shift expected for a purely phenolic tautomer, with very minor changes upon changing the substituent R. An exception is carbon C-7, but in this case the sign and magnitudes of the changes are mainly derived from the intrinsic SCS effects discussed above: R = NO_2, +2.73 ppm; R = MeO, −2.22 ppm (Table 1). Upon lowering the temperature (Table 2), only slight shifts in the equilibrium-sensitive carbons of compound **3** were observed, in agreement with the fact that it mainly exists in form **e**. It should be noticed that a shift towards **f** was previously reported for electron-donating R group on the basis of the absorption spectra of these compounds in solution.[10] Interestingly, the sense of this latter effect is opposite to that observed in arylazonaphthols, and has been explained as a result of the increased basicity of the proton accepting nitrogen when R increases its donating ability.[10]

On the other hand, chemical shifts reported in Table 1 for derivatives of 2-hydroxynaphthalene-1-carbaldehyde **6–10** are all indicative that appreciable amounts of both tautomers exist at equilibrium in this case. In particular, C-2 is considerably deshielded with respect to the same carbon in compounds **1–5**. The use of eqn. (1) allows a crude estimation of equilibrium constants to be obtained (see Table 1), and, analogously to the case of compounds **1–5**, leads to a negligible equilibrium shift on changing the electronic demand of R. Comparing the results for compounds **1–5** with those for compounds **6–10** shows that several other carbons have been affected by the change from an almost pure **e** tautomer to a **g–h** mixture in which **h** is predominant. As expected, C-1′, C-1 and C-11 are considerably shielded with respect to analogous carbons (C-1′, C-1 and C-7) in salicylidene anilines, whereas carbon C-4 is relatively deshielded. The chemical shift observed for C-1 throughout the series is rather surprising for an aromatic quaternary carbon, but may be explained as the result of a significant contribution of the enamine form **h**. Overall, no appreciable changes in the equilibrium-sensitive chemical shifts are observed upon changing the substituent R, with the exception of C-11. In this latter case, however, the sign and magnitudes of the changes suggest that they may again be due to intrinsic SCS effects: R = NO_2, +2.95 ppm; R = MeO, −0.5 ppm (Table 1).

Table 2 shows variable temperature results on compound **8**. In contrast with compound **3**, significant changes are now observed in the chemical shifts which are sensitive to the

Table 1 Solution ($CDCl_3$) ^{13}C NMR spectroscopic data for Schiff bases and K_{eq} calculated from eqn. (1)

	Compound									
Carbon	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1	119.21	119.18	118.97	118.79	118.56	108.51	108.58	108.47	108.95	109.27
2	160.70	160.77	160.90	161.10	161.15	169.83	169.26	171.16	170.93	169.16
3	116.80	116.92	117.00	117.23	117.36	118.57	118.66	118.58	118.78	118.94
4	131.79	132.47	132.90	133.73	134.34	135.39	135.88	136.79	137.48	137.73
5	118.62	118.79	118.84	119.18	119.41	126.87	127.06	126.98	127.25	127.58
6	131.35	131.78	132.09	132.56	132.87	122.85[b]	123.15[b]	123.34[b]	123.80[b]	124.15[b]
7	157.75	160.20	162.42	164.05	165.25	122.31[b]	121.88[b]	122.42[b]	122.07[b]	121.30[b]
8						127.52[c]	127.72[c]	126.32[c]	128.23[c]	128.47[c]
9						129.06[c]	129.13[c]	129.20[c]	129.34[c]	129.50[c]
10						133.00	132.96	133.12	132.95	132.83
11						150.91	153.39	153.89	154.64	156.84
1′	136.76	141.11	148.20	152.36	154.04	133.51	138.20	144.49	148.98	151.78
2′,6′	122.00	122.10	120.95	121.19	121.74	121.00	121.31	119.94	119.92	120.79
3′,5′	112.51	114.40	129.17	129.72	125.05	112.72	114.67	129.51	130.02	125.40
4′	149.68	158.63	126.68	135.17	145.92	149.21	158.32	127.93	134.61	145.49
K_{eq}	—[a]	—[a]	—[a]	—[a]	—[a]	1.5	1.3	1.8	1.8	1.3

[a] These compounds exist as the phenolic tautomer **e**. [b,c] Assignments within one column may be interchanged.

Table 2 Chemical shifts at variable temperature for compounds **3** and **8** and values of K_{eq} calculated with eqn. (1)

	Compound **3**, T/K				Compound **8**, T/K			
Carbon	291	271	251	231	291	271	251	231
1	118.97	118.85	118.63	118.50	108.47	108.16	107.82	107.47
2	160.90	160.70	160.48	160.30	171.16	172.32	173.43	175.00
3	117.00	116.90	116.78	116.70	118.58	118.42	118.24	118.10
4	132.90	132.90	132.86	132.84	136.79	137.11	137.40	137.83
5	118.84	118.85	118.84	118.84	126.98	126.70	126.41	126.14
6	132.09	132.08	132.05	132.03	123.34[b]	123.30[b]	123.22[b]	123.17[b]
7	162.42	162.40	162.36	162.33	122.42[b]	122.22[b]	123.22[b]	123.68[b]
8					126.32[c]	126.28[c]	126.21[c]	126.14[c]
9					129.20[c]	129.18[c]	129.13[c]	129.33[c]
10					133.12	132.96	132.84	132.78
11					153.89	153.14	152.35	151.38
1′	148.20	147.93	147.68	147.49	144.49	143.62	142.75	141.74
2′,6′	120.95	120.94	120.91	120.89	119.94	119.70	119.41	119.10
3′,5′	129.17	129.15	129.11	129.08	129.51	129.51	129.49	129.51
4′	126.68	126.69	126.67	126.66	127.93	127.93	127.92	127.94
K_{eq}	—[a]	—[a]	—[a]	—[a]	1.8	2.3	2.8	4.0

[a] These compounds exist as the phenolic tautomer **e**. [b,c] Assignments within one column may be interchanged.

equilibrium **g** $\rightleftharpoons$ **h**, *i.e.* C-1′, C-11, C-1, C-4 and C-2. All the changes are consistent with a shift towards tautomer **h** on cooling, in agreement with the fact that the room temperature equilibrium mixture is enriched in **h** with respect to **g** (Table 2). Estimation of the equilibrium constants at different temperatures with the aid of eqn. (1) (Table 2) yields the following parameters: $\Delta H^0 = -7.3 \pm 0.1$ kJ mol^{-1}, $\Delta S^0 = -20.2 \pm 0.3$ J mol^{-1} K^{-1}, which should however be taken with caution due to the approximations involved. One conclusion to be drawn from this result is that the addition of a second aromatic ring (in going from **1–5** to **6–10**) causes the equilibrium to be shifted to the keto form **h**. Furthermore, it strongly supports the idea of a fast proton transfer reaction between **g** and **h**, which, as in similar cases, is likely to occur in the solid state. This may be in contrast with previous claims derived from X-ray crystallographic analysis of related Schiff bases which seemed to support a unique structure with the labile hydrogen more or less centred between the nitrogen and oxygen.[8]

We now discuss the results obtained by applying the semi-empirical MO program AM1 to the compounds studied. These calculations are routinely used to study molecules capable of forming strong hydrogen bonds.[15] The study of the relative stability of prototropic tautomers in solution requires that one takes into account differences in solvation energies for each tautomer. This has been previously done by modifying AM1 to handle interactions between the molecules studied and the solvent.[16] It has been found that the equilibria are affected by differential solvation provided a significant difference exists in the dipole moments of the tautomers involved.[16] In all compounds studied in the present work, the differences in dipole moments between both tautomers were rather small, prompting us to evaluate the performance of AM1 with no correction for solvation.

Full geometry optimization was carried out for compounds **1–10** with the results presented in Table 3. Calculated bond lengths around the six-membered H-chelated ring for both tautomers show alternation between formally double and single bonds, with lengths which are in agreement with those reported in the literature from X-ray diffraction data for compounds which are representative of extreme tautomeric structures. For instance, the observed bond distances within the intramolecularly hydrogen bonded ring in the related compound bis-salicylidene-*p*-phenylenediamine (BSP) are C-2–O, 1.356 Å; C-1–C-2, 1.419 Å; C-1–C-7, 1.442 Å and C-7–N, 1.283 Å,[8a] whereas the (average) calculated values are 1.36 Å, 1.41 Å, 1.46 Å and 1.29 Å, respectively (Table 3). One conclusion that can

Table 3 Relevant AM1 parameters for the compounds studied

	Bond distances[a]/Å				
Compound	N–C	C–C	C–C	C–O	ΔH_f^0/kJ mol^{-1}
1e	1.292	1.466	1.408	1.367	159.0
1f	1.352	1.388	1.463	1.252	177.8
2e	1.292	1.465	1.409	1.366	−33.9
2f	1.354	1.386	1.464	1.252	−15.9
3e	1.292	1.465	1.408	1.366	122.6
3f	1.355	1.385	1.464	1.251	140.6
4e	1.293	1.464	1.408	1.366	−30.8
4f	1.359	1.383	1.466	1.251	−14.8
5e	1.294	1.462	1.409	1.365	139.7
5f	1.364	1.380	1.469	1.250	156.9
6g	1.292	1.468	1.390	1.368	23.4
6h	1.355	1.387	1.464	1.250	19.2
7g	1.292	1.467	1.390	1.368	50.2
7h	1.357	1.385	1.465	1.250	46.0
8g	1.292	1.467	1.390	1.367	208.4
8h	1.358	1.384	1.466	1.250	201.7
9g	1.293	1.465	1.391	1.366	54.0
9h	1.363	1.381	1.468	1.249	46.7
10g	1.295	1.463	1.393	1.364	225.9
10h	1.368	1.377	1.472	1.248	216.7

[a] These bond distances correspond to the six-membered H-chelated ring.

be gathered from Table 3 is that AM1 predicts a proton motion within a double minimum potential energy profile, since in none of the cases studied the labile proton is centred, but it is always found bonded either to the oxygen or the nitrogen atom. As to the relative energies of both tautomers, AM1 predicts that in the case of salicylidene anilines, form **e** will be significantly more stable than **f** (about 17–19 kJ mol^{-1}), whereas for anils of 2-hydroxynaphthalene-1-carbaldehyde the preferred form is the keto structure **h**. In the latter case, however, the differences in ΔH_f^0 are small (4–9 kJ mol^{-1}) and therefore may easily be interpreted as allowing the existence of both tautomers in equilibrium. In fact, the value of ΔH^0 predicted for compound **8** (-6.7 kJ mol^{-1}) is in excellent agreement with that found by NMR spectroscopy. The overall results are thus in good agreement with the experimental ones discussed above, even when the complications arising from differential solvation energies have been neglected. As seen in Table 3, only slight changes in the relative enthalpies of formation of both tautomers is obtained upon varying the nature of R, again in agreement with the carbon NMR spectroscopic results. Interestingly, AM1 predicts that these small changes are (both in compounds **1–5** and **6–10**) in the direction of increasing the amount of the keto form with electron-withdrawing substituents, as in arylazonaphthols, but in clear disagreement with early UV absorption data. This point may require further work to be ascertained.

In conclusion, both variable-temperature ^{13}C NMR spectroscopic information and semi-empirical AM1 calculations support the existence of 2-hydroxy-1-naphthylidene anilines as a rapidly interconverting equilibrium mixture of phenolic and quinonoid tautomers. The populations of these tautomers can be estimated from the ^{13}C NMR chemical shifts of the C–O carbon, and significant contents of both are obtained, with the quinonoid tautomer being the preferred one.

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