X-Ray Crystallographic Analysis of the NH Form of a Salicylideneaniline at 15 K

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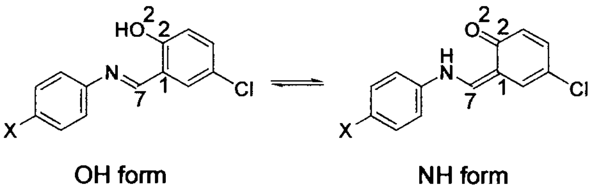
The structure of the NH form of a salicylideneaniline was determined by X-ray crystallographic analysis of *N*-(5-chloro-2-hydroxybenzylidene)-4-hydroxyaniline at 15 K. Comparison of the X-ray structure with the structure obtained from quantum mechanical calculations using density functional theory revealed that the NH form is predominantly zwitterionic in crystals and predominantly quinoidal in gas phase.

Proton tautomerization plays an important role in many fields of chemistry and biochemistry.[1,2] The tautomerization in salicylideneanilines (eq 1) is a subject of particular interest, because it is closely related to photo- and thermochromism.[3,4] Extensive studies have revealed that the enol or OH form is much more stable than the keto or NH form. The OH form has been well characterized by spectroscopic and crystallographic studies.[5,6] In contrast, the NH form has been much less characterized. Although a few crystal structures were reported as of the NH form,[7,8] whether these crystals contain exclusively the NH form has remained uncertain due to the lack of temperature dependent experiments. Recently we have observed a crystal structure change associated with the tautomerization as a dynamic disorder in the crystals of *N*-(5-chloro-2-hydroxybenzylidene)-4-hydroxyaniline (**1**), where the NH form is greatly stabilized by intermolecular hydrogen bonding and becomes slightly more stable than the OH form.[9] It is therefore expected that the NH form should be exclusively populated at sufficiently low temperature. We report here the molecular structure of the NH form on the basis of the X-ray crystallographic analysis of **1** at 15 K. This is the first structure determination of a pure NH form of a salicylideneaniline.



(1)

1 : X = OH **2** : X = H

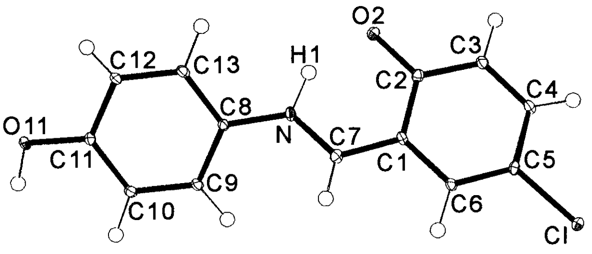


Figure 1. Perspective view of **1** at 15 K. The ellipsoids are drawn at the 50% probability level.

Figure 1 shows a perspective view of the molecule of **1** at 15 K. Table 1 lists selected geometrical parameters obtained from the X-ray crystallographic analyses of **1** at 90 and 15 K.[10] For comparison Table 1 also lists geometrical parameters of **2**, which exists exclusively as the OH form in crystals.[6]

As shown in Figure 1, the observed molecular structure of **1** at 15 K is of the NH form. The difference Fourier synthesis confirms the existence of the hydrogen atom connected to N but not to O2.[11]

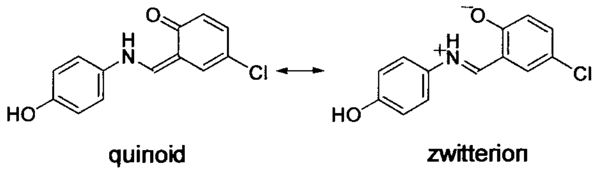
The fact that the NH form is exclusively populated at 15 K in the crystals of **1** is also confirmed as follows. In the crystals of **1**, which have an unresolved disorder between the NH and OH forms at higher than 90 K, each of the observed bond lengths is the weighted average of the corresponding length of two forms according to their populations and hence is expected to vary with temperature.[9] However, there is no significant difference in bond length between 90 and 15 K; i.e., the disorder disappears at lower than 90 K. The results therefore indicate that the equilibrium completely shifts to the NH form at 15 K.

The NH form can be regarded as a resonance hybrid of two canonical structures, the quinoid and zwitterionic forms (eq 2). Which canonical structure is dominant has been a matter of considerable interest.[7,12]

Table 1. Selected geometrical parameters

Compd	Method	T/K	Form	Distance /Å			
				O2–C2	C2–C1	C1–C7	C7–N
1	XRD	90^a	NH	1.310(1)	1.433(2)	1.425(1)	1.308(1)
	XRD	15^b	NH	1.312(3)	1.434(3)	1.422(3)	1.312(3)
	DFT	0^b	OH	1.341	1.423	1.452	1.292
	DFT	0^b	NH	1.263	1.469	1.400	1.330
2	XRD	90^a	OH	1.350(2)	1.412(3)	1.457(3)	1.291(2)
	DFT	0^b	OH	1.340	1.423	1.452	1.291
	DFT	0^b	NH	1.262	1.470	1.398	1.332

[a] Reference 9. [b] This study.



(2)

The observed molecular structure of the NH form of **1** is significantly different from that expected for a typical quinoid form. The O2–C2 and C1–C7 bonds are considerably longer than would be expected[13] for standard C=O [1.222 Å] and C=C [1.340 Å] bonds in conjugated enones, respectively. Furthermore, C2–C1 is considerably shorter than a standard C–C bond [1.464 Å] in conjugated enones, and C7–N1 is shorter than a standard C(sp^3)–N bond [1.355 Å] in enamines. Thus, the NH form in the crystals of **1** is considerably zwitterionic.

The molecular structure of the NH form in the crystalline state is considerably different from that in the gas phase. The structures in the gas phase were obtained from quantum mechanical calculations using density functional theory (DFT) for the free molecules of **1** and **2** (Table 1).[14] The calculations for the NH form show that the length of the O2–C2 bond is closer to the standard length of the C=O bond [1.222 Å] in conjugated enones rather than to that of the C–O bond [1.362 Å] in phenols. Thus, the NH form is predominantly quinoidal in the gas phase and predominantly zwitterionic in crystals.

The molecular structure of the OH form is, in contrast, nearly the same in the crystalline state and the gas phase. The X-ray structure of the OH form of **2** agrees well with the structure obtained from DFT calculations (Table 1).

The DFT calculations show that the NH form is less stable than the OH form in the gas phase and that the relative instability of the NH form is nearly the same between **1** and **2** in the gas phase. The energy difference between the two forms is ca. 3.9 kcal mol^{-1} for **1** and ca. 4.1 kcal mol^{-1} for **2**. By contrast, the stability of the NH form in crystals is much different from that in the gas phase. The NH form is less stable than the OH form by ca. 1.8 kcal mol^{-1} for **2**,[5,15] which does not have intermolecular hydrogen bonding, and it is more stable than the OH form by ca. 0.4 kcal mol^{-1} for **1**,[16] which has intermolecular hydrogen bonding. The results show that the NH form is considerably stabilized in crystals even without intermolecular hydrogen bonding[17] and much more stabilized when intermolecular hydrogen bonding is present.

The stabilization of the NH form can be ascribed to the increase in the zwitterionic character of the NH form in crystals, by which the molecules would become more polar; the electrostatic intermolecular interactions would become stronger; and intermolecular hydrogen bonding would be strengthened.

In summary, we succeeded for the first time in determination of the molecular structure of the pure NH form and revealed that the NH form is predominantly zwitterionic in crystals and predominantly quinoidal in gas phase.

References and Notes

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10 The diffraction measurements at 15 K were made on a Huber off-center type 511.1/424 diffractometer with Mo Kα (λ = 0.71073 Å). The temperature was held constant within ± 2 K during the measurement using a cryostat APD-Cryogenics DE201. Reflections having intensity greater than $5\sigma_F$ were used for the structure refinement, because weaker reflections were hidden by the scattering from the shroud of the cryostat. Crystal data for **1**: $C_{13}H_{10}ClNO_2$, MW = 247.67, monoclinic, space group $P2_1/a$, $Z = 4$, λ(Mo, Kα) = 0.71073 Å. T = 15 K: a = 7.018(1), b = 12.419(4), c = 12.473(3) Å, β = 91.66(2) °, V = 1086.5(5) $Å^3$, Z = 4, ρ_{calcd} = 1.514 gcm^{-3}, μ = 0.338 mm^{-1}, 2562 unique reflections ($\geq 5\sigma_F$), R = 0.0476.

11 The difference Fourier synthesis was carried out for the refined structure that has all the atoms except the tautomeric hydrogen atom. The distance between N and H1 was 0.97(5) Å, and that between O2 and H1 was 1.66(5) Å.

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