Tautomerism of a Nitro Derivative of *N*-Salicylideneaniline in Crystals

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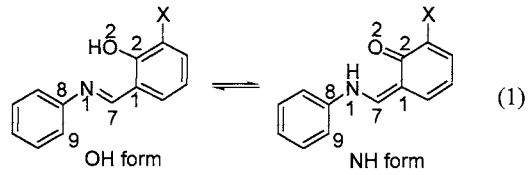
(Received April 5, 1999; CL-990252)

X-Ray crystallographic and electronic absorption spectroscopic studies on *N*-(2-hydroxy-3-nitrobenzylidene)aniline revealed that this compound exists as a mixture of the OH and NH forms with nearly the equal populations in crystals.

N-Salicylideneanilines belong to a class of the popular compounds which show thermo- or photochromism in crystals.[1] Extensive studies have revealed that the chromisms are closely related to the tautomerism between the OH and NH forms [equation (1)].[2] The tautomerism has recently been evidenced by X-ray diffraction as a dynamic disorder in crystals.[3] Most of *N*-salicylideneanilines including the parent compound (**1**) greatly favor the OH form in both crystals and solutions. However, it has been noted that if a nitro group is introduced into the benzene ring of the salicylaldehyde part, the tautomeric behavior is changed significantly.[4,5] For example, it was reported that *N*-(2-hydroxy-3-nitrobenzylidene)aniline (**2**) exists as the OH form in saturated-hydrocarbon solvents at room temperature but exists as an aggregate at 77 K where the NH form is involved.[5] The behavior of **2** in crystals has, however, remained unknown. This paper reveals the tautomerism of **2** in crystals on the basis of X-ray crystallography and electronic spectroscopy.



(1)

1:X=H **2**:X=NO_2

X-Ray diffraction measurements of the crystals of **2** were carried out at 90, 160, 220, and 297 K.[6] Selected geometrical parameters are listed in Table 1. A perspective view of the molecule at 90 K is shown in Figure 1.

Table 1. Selected bond lengths of **2** (/Å)

T/K	O2–C2	C2–C1	C1–C7	C7–N1
297	1.313(2)	1.423(3)	1.437(3)	1.283(3)
220	1.304(2)	1.426(2)	1.438(2)	1.288(2)
160	1.306(2)	1.425(2)	1.442(2)	1.288(2)
90	1.303(2)	1.432(2)	1.446(2)	1.287(2)

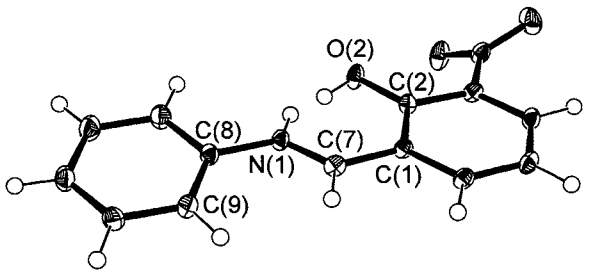


Figure 1. Perspective view of **2** at 90 K. The ellipsoids are drawn at the 50 % probability level.

Figure 1 shows that the tautomeric hydrogen atom is located on both O2 and N1 atoms. Thus, the observed structure is the superposition of the OH and NH forms which are unresolved except for the tautomeric hydrogen atom. This disorder was always observed at higher temperatures up to 297 K.

Figure 2 shows a difference electron density map at 90 K to demonstrate the disorder clearer. This map was obtained from the difference Fourier synthesis using the refined structure from which only the tautomeric hydrogen atom was removed. The map clearly locates two peaks assigned to two hydrogen atoms, one connected to O2 and the other to N1.

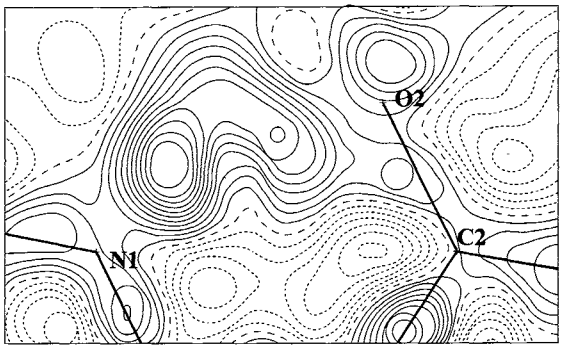


Figure 2. A difference electron density map in the plane of N(1)–C(2)–O(2) at 90 K. Contour interval 0.05 eÅ^{-3}, negative contours dotted, zero contour dashed, positive contours solid.

Essentially the same maps were obtained from the structure at all the observed temperatures. The observed bond lengths did not change significantly with variation of the temperature (Table 1). The results indicate that the OH and NH forms are nearly equally populated and therefore have nearly the same stability in the crystals.

The crystal structure does not show any van der Waals contact or intermolecular hydrogen bonding. It has been noted that the NH form of *N*-salicylideneanilines is greatly stabilized by intermolecular hydrogen bondings.[3,7] There are few cases where the NH form is substantially populated without intermolecular hydrogen bonding.[8] The results shown here correspond to the latter case.

Figure 3 shows electronic spectra of **2** in crystals and in 3-methylpentane solution at room temperature. The spectrum in the solution shows an absorption maximum at 350 nm, which was assigned to the OH form.[5] The spectrum in the crystals shows three absorption bands A, B, and C: the band A appears as a shoulder at ca. 480 nm; the band B appears as the maximum at ca. 460 nm; the band C appears as a shoulder at 360 nm. This spectrum is consistent with the X-ray results. Electronic transition energies of the OH and NH forms of **2** were calculated by the INDO/S-CI method[9,10] using the molecular structures

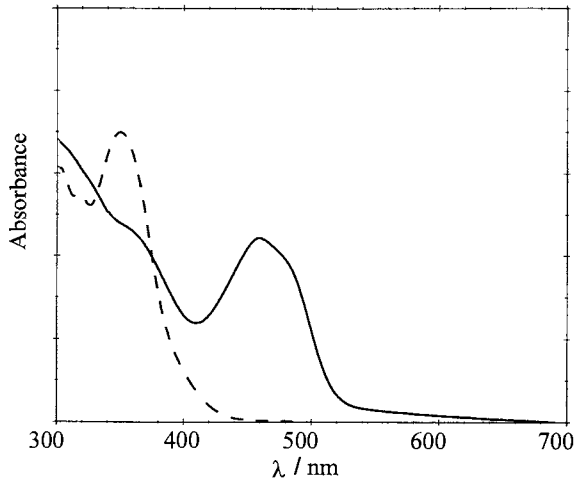


Figure 3. Electronic spectra of **2**. Solid line: in a thin KBr disk, λ_{max} = 460 nm. Broken line: in 3-methylpentane, λ_{max} = 350 nm, $\varepsilon = 9.94 \times 10^3$ ($c = 7.05 \times 10^{-5}$ mol L^{-1}).

from the X-ray analysis. The OH form has the lowest energy transition at 358 nm with the oscillator strength of 0.42. The NH form has the lowest and the next lowest energy transitions at 476 nm with the oscillator strength of 0.23 and at 452 nm with the oscillator strength of 0.17.[11] Therefore, the bands A and B are assigned to the NH form and the band C is assigned to the OH form. Thus, the electronic spectra of **2** in the crystals are interpreted as the superposition of the absorption from the OH and NH forms.

The tautomeric behavior of **2** is remarkable for two points; the difference in the behavior from the parent compound **1** and the difference between the crystals and the solution. To explain these points, the quantum mechanical calculations using the density functional theory (DFT)[12] was carried out for free molecules of **1** and **2**.

The difference in the behavior from **1** can be explained by considering the electronic effect of the nitro group. It increases the acidity of the OH group and destabilizes the OH form of **2** considerably. The DFT calculations show that the NH form is less stable than the OH form by 4.6 kcal mol^{-1} for **1** and 2.9 kcal mol^{-1} for **2**. The difference of 1.7 kcal mol^{-1} may be interpreted as a measure of the destabilization of the OH form of **2** due to the electronic effect of the nitro group.

The difference between the crystals and the solutions can be explained by considering the packing effect to the conformations of the molecules in crystals. It is assumed that molecules adopt the most stable conformation in solutions. According to the DFT calculations, the torsion angle of C7–N1–C8–C9, ω_1, is 33.1° for the most stable conformation of OH form of **2**. The most stable conformation of the NH form is nearly planar (ω_1 = 12.9°). On the other hand, nearly the planar conformation [ω_1 = −7.7(2)°] is adopted by the OH form as well as the NH form in the crystals. The basicity of the imine nitrogen atom N1 is larger in the planar conformation than in the twisted conformation because the lone pair electrons of N1 cannot be conjugated with the benzene rings in the planar conformation. The OH form is, therefore, destabilized by the planarization. The destabilization energy, which is estimated as the energy difference between the planar and the twisted OH form, amounts to *ca.* 1.4 kcal mol^{-1} from the DFT calculations. Thus, the energy difference between the OH and NH forms is considerably smaller in the crystals than in the solution. It is therefore concluded that both the electronic effect of the nitro group and the packing effect to the conformations of the molecules substantially contribute to nearly the same stability of the OH and NH forms in the crystals of **2**.

References and Notes

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6 Crystal data for **2**: $C_{13}H_{10}N_2O_3$, *MW* = 242.23, recrystallized from methanol, Mp. 408 K, orthorhombic, space group *Pccn*, Mo *Kα*(λ = 0.71073 Å). *T* = 297 K: *a* = 23.845(4), *b* = 7.099(3), and *c* = 13.539(4) Å, *V* = 2291.7(2) Å^3, *Z* = 8, ρ_{calcd} = 1.404 gcm^{-3}, μ = 0.102 mm^{-1}, 2628 unique reflections, *R* = 0.0576. *T* = 220 K: *a* = 23.739(3), *b* = 7.040(2), and *c* = 13.510(2) Å, *V* = 2257.6(7) Å^3, *Z* = 8, ρ_{calcd} = 1.425 gcm^{-3}, μ = 0.104 mm^{-1}, 2595 unique reflections, *R* = 0.0459. *T* = 160 K: *a* = 23.672(3), *b* = 6.994(2), and *c* = 13.493(2) Å, *V* = 2233.9(8) Å^3, *Z* = 8, ρ_{calcd} = 1.440 gcm^{-3}, μ = 0.105 mm^{-1}, 2566 unique reflections, *R* = 0.0418. *T* = 90 K: *a* = 23.617(2), *b* = 6.939(1), and *c* = 13.475(2) Å, *V* = 2208.2(6) Å^3, *Z* = 8, ρ_{calcd} = 1.457 gcm^{-3}, μ = 0.106 mm^{-1}, 2527 unique reflections, *R* = 0.0485. All the hydrogen atoms at any observed temperature were located from difference maps.
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10 The INDO/S-CI calculations were carried out by using WinMOPAC Ver. 2.0.
11 The configuration interaction (CI) consisted of 1600 selected single excitations. The main character of the transition at 358 nm for the OH form is a single electron transition from the HOMO to LUMO (51%). The main characters of the transitions at 476 and 452 nm for the NH form are also single electron transitions from the HOMO to LUMO (51 and 39%, respectively).
12 The calculations were carried out at Becke3LYP/6-31G** level using Gaussian94.