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Crystal Structure Change for the Thermochromy of *N*-Salicylideneanilines. The First Observation by X-ray Diffraction

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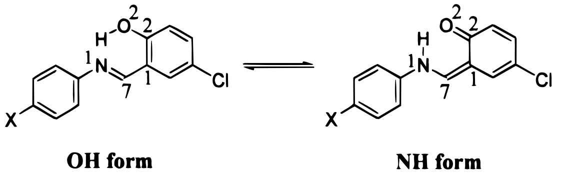
Reversible change in color of substances with variation of the temperature is known as thermochromism and has attracted much interest from chemists for a long time.[1] *N*-Salicylideneanilines belong to a class of the most popular thermochromic compounds.[2] For example, the crystals of *N*-(5-chloro-2-hydroxybenzylidene)aniline (**1**) are orange-red at room temperature and pale yellow at 77 K, and their color changes reversibly with variation of temperature.[3] Extensive studies have revealed that the thermochromism of *N*-salicylideneanilines originates from the tautomerism between the OH and NH forms.[4] A change in the crystal structure for their thermochromy has, however, never been observed, although an attempt to do so was reported for **1** by Bregman et al.[5] We wish to report the first observation of a crystal structure change for the thermochromy of *N*-salicylideneanilines, using variable temperature X-ray analysis of *N*-(5-chloro-2-hydroxybenzylidene)-4-hydroxyaniline (**2**).[6]



(1)

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

Perspective views of the molecule of **2** are shown in Figure 1. Selected bond lengths obtained from the X-ray crystallographic analyses of **2**[7] are listed in Table 1. Bond lengths of **1**,[8] which are regarded as of the pure OH form,[9] are also listed in Table 1 for comparison.

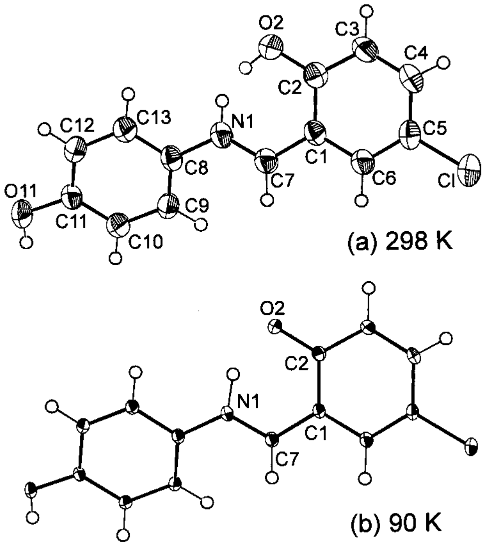
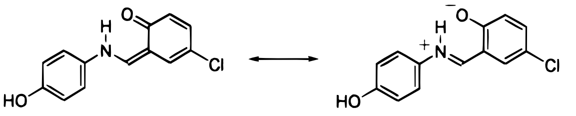


Figure 1. Perspective views of **2** with the atom numbering scheme: (a) at 298 K and (b) at 90 K. The ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths of **1** and **2** (Å)

compd	*T* (K)	O2−C2	C2−C1	C1−C7	C7−N1
1	90	1.350(2)	1.412(3)	1.457(3)	1.291(2)
2	375	1.320(2)	1.414(3)	1.434(3)	1.288(3)
	298	1.321(2)	1.422(3)	1.433(2)	1.293(2)
	220	1.318(2)	1.427(2)	1.428(2)	1.297(2)
	160	1.313(2)	1.427(2)	1.429(2)	1.303(2)
	90	1.310(1)	1.433(2)	1.425(1)	1.308(1)



(2)

2k **2ki**

Table 1 shows that the length of each of the bonds which could change in bond order by the tautomerism is significantly different between **1** and **2**. Thus, O2−C2 bond of **2** is shorter than that of **1** and C1−C7 bond of **2** is also shorter than that of **1**; C2−C1 bond of **2** is longer than that of **1** and C7−N1 bond of **2** is also longer than that of **1**. The results suggest that the NH form might coexist in the crystals of **2**.

The most important point is that lengths of these bonds of **2** systematically vary with the temperature. Thus, the lengths of

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(1) Review: (a) Day, J. H. *Chem. Rev.* **1963**, *63*, 65−80. (b) Nassau, K. *The Physics and Chemistry of Color*; John Wiley and Sons: New York, 1983; pp 132−133, 347−348.

(2) Review: (a) Hadjoudis, E.; Vittorakis, M.; Moustakali-Mavridis, I. *Tetrahedron* **1987**, *43*, 1345−1360. (b) Hadjoudis, E. Tautomerism by Hydrogen Transfer in Anil, Aci-Nitro and Related Compounds. In *Photochromism*; Dürr, H., Bouas-Laurent, H., Eds.; Studies in Organic Chemistry 40; Elsevier: Amsterdam, 1990; pp 685−712. (c) Inabe, T. *New J. Chem.* **1991**, *15*, 129−136. (d) E. Hadjoudis, E. *Molecular Eng.* **1995**, 5, 301−337.

(3) (a) Cohen, M. D.; Schmidt, G. M. *J. Phys. Chem.* **1962**, *66*, 2442−2445. (b) Cohen, M. D.; Schmidt, M. J.; Flavin, S. *J. Chem. Soc.* **1964**, 2041−2051.

(4) (a) Dudek, G. O.; Dudek, E. P. *J. Am. Chem. Soc.* **1966**, *88*, 2407−2412. (b) Becker, R. S.; Richey, W. F. *J. Am. Chem. Soc.* **1967**, *89*, 1298−1302. (c) Hadjoudis, E.; Milia, F.; Seliger, J.; Blinc, R.; Zagar, V. *Chem. Phys.* **1980**, 47, 105−109. (d) Inabe, T.; Gautier-Luneau, S.; Hoshino, N.; Okaniwa, K.; Okamoto, H.; Mitani, T.; Nagashima, U.; Maruyama, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 801−810. (e) Inabe, T.; Luneau I.; Mitani, T.; Maruyama, Y.; Takeda, S. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 612−621. (f) Wozniak, K.; He, H.; Klinowski, J.; Jones, W.; Dziembowska, T.; Grech, E. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 77−85. (g) Katritzky, A. R.; Ghiviriga, I.; Leeming, P.; Soti, F. *Magn. Reson. Chem.* **1996**, *34*, 518−526. (h) Alarcón, S. H.; Olivieri, A. C.; Nordon, A.; Harris, R. K. *J. Chem. Soc., Perkin 2* **1996**, 2293−2296. (i) Sekikawa, T.; Kobayashi, T.; Inabe, T. *J. Phys. Chem. A.* **1997**, *101*, 644−649.

(5) Bregman, J.; Leriserowitz, L.; Schmidt, G. M. *J. Chem. Soc.* **1964**, 2068−2085.

(6) Compound **2** was prepared by the condensation of 5-chlorosalicylaldehyde with *p*-aminophenol in methanol at room temperature. Single crystals for the X-ray measurement were obtained via a slow evaporation of methanol solution at room temperature. Mp 516−517 K.

(7) Crystallographic data for **2**: $C_{13}H_{10}ClNO_2$, MW = 247.67, monoclinic, space group $P2_1/a$, $Z = 4$, λ(Mo, Kα) = 0.71073 Å. T = 375 K, a = 7.2240(3), b = 12.6908(8), c = 12.5188(7), β = 93.606(5)°, V = 1145.4(1) Å^3, R = 0.0486, GOF = 0.991. T = 298 K, a = 7.1805(4), b = 12.638(1), c = 12.514(1), β = 93.184(7)°, V = 1133.9(2) Å^3, R = 0.0430, GOF = 0.991. T = 220 K, a = 7.119(2), b = 12.563(2), c = 12.490(2), β = 92.71(2)°, V = 1115.8(4) Å^3, R = 0.0469, GOF = 0.996. T = 160 K, a = 7.086(2), b = 12.518(2), c = 12.485(2), β = 92.42(2)°, V = 1106.5(4) Å^3, R = 0.0458, GOF = 1.033. T = 90 K, a = 7.043(2), b = 12.459(3), c = 12.4827(19), β = 92.031(18)°, V = 1094.7(4) Å^3, R = 0.0388, GOF = 1.057.

(8) The X-ray structure of **1** was redetermined with higher accuracy in this study. Our structure was essentially identical with that determined by Bregman et al. The crystallographic data: $C_{13}H_{10}ClNO$, MW = 231.67, orthorhombic, space group $Pca2_1$, $Z = 4$, λ(Mo, Kα) = 0.71073 Å. T = 298 K, a = 12.177(3), b = 4.483(3), c = 19.271(3), V = 1051.9(7) Å^3, R = 0.0350, GOF = 1.042.

(9) It was proved by Schmidt and co-workers that **1** exists exclusively as the OH form at 90 K in crystals.[3,]

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Table 2. Populations of the NH and OH Forms in the Crystals of **2**

	populations (%)			
	from electronic spectra		from X-ray analysis[a]	
T (K)	OH form	NH form	OH form	NH form
90	11	89	10	90
160	19	81	17	83
220	27	73	26	74
299	37	63	31	69

[a] Estimated from the length of O2−C2 bond determined by X-ray crystallographic analysis. Estimations from the other lengths gave essentially the same results.

C2−C1 and C7−N1 bonds increase and the lengths of O2−C2 and C1−C7 bonds decrease with lowering the temperature. The results are interpreted as follows: (i) The observed structure is the superposition of the OH and NH forms, which remain unresolved. (ii) Each of the observed bond lengths is the weighted average of the corresponding length of the OH and NH forms according to the population of two forms. (iii) Their populations vary with the temperature. As a result, the observed structure changes with variation of the temperature. It is therefore concluded that there is an equilibrium between the OH and NH forms in crystals and that the population of the NH form increases with lowering the temperature.

This conclusion becomes definitive from the difference Fourier synthesis using the refined structure from which only the tautomeric hydrogen atom is removed. The difference synthesis for the structure at 160 K or higher locates two peaks assigned to two hydrogen atoms, one connected to O2 and the other to N1. In contrast, the difference synthesis for the structure at 90 K locates only a single peak assigned to the hydrogen atom connected to N1. Accordingly, the two hydrogen atoms were treated as disordered in the refinement of structures at 160 K or higher [Figure 1a], whereas the structure at 90 K was refined as the pure NH form [Figure 1b]. Thus, the X-ray diffraction unambiguously displayed the occurrence of the tautomerism that favors the NH form in crystals.

Electronic spectra show that the crystals of **2** are thermochromic. The absorption band at 485 nm, which is assigned to the NH form, appears at room temperature and increases in intensity with the lowering the temperature. The results are consistent with those from X-ray diffraction: the NH form exists appreciably in the solid state at room temperature and increases in population with lowering the temperature. The change in the X-ray structure of **2** with variation of the temperature is, therefore, certainly for the thermochromy.

The populations of the NH and OH forms at different temperatures were estimated from the temperature dependence of the intensity of the absorption band (Table 2), by the use of the method reported by Theilacker et al.[10] Almost the same results were also obtained by the application of a similar method to the temperature dependence of the bond lengths which were determined by X-ray crystallographic analyses (Table 2). The results reveal that ca. 90% of **2** exists as the NH form in crystals at 90 K and that the energy difference between the NH and OH forms is small in crystals.

The geometry of **2** at 90 K is significantly different from that expected for a typical "keto" form **2k**. The length of O2−C2 bond and that of C1−C7 bond are considerably longer than the standard length of the C═O bond [1.222 Å] and that of C═C bond [1.340 Å] in conjugated enones,[11] respectively, and the length of C2−C1 and that of C7−N1 bond are considerably shorter than the standard length of the C−C bond [1.464 Å] in conjugated enones and that of C(sp^2)−N bond [1.355 Å] in enamines, respectively. The results suggest that the NH form in the crystals of **2** has the character of the zwitter ion **2ki** considerably.

In contrast to the crystalline state, **2** favors the OH form in solution. This was evidenced by electronic spectra. The spectra of the EPA solution[12] show no absorption band for the NH form at ca. 485 nm in the temperature range from 298 to 77 K. The results show that **2** exists exclusively as the OH form in the solution. The stabilization of the NH form in crystals is, therefore, ascribed to intermolecular interactions.

Examinations of the molecular packing of the crystals of **2** reveal the occurrence of the intermolecular hydrogen bonding. The distance between O2 and H11 of the adjacent molecule was 2.622(1) Å and the angle of O2···H11−O11 was 178(2)° at 90 K.[13,14] It is therefore concluded that the stabilization of the NH form in the crystals of **2** results primarily from the intermolecular hydrogen bonding in crystals.

In summary, we succeeded for the first time in the observation of the crystal structure change for the thermochromy of salicylideneanilines by the X-ray diffraction of **2** and demonstrated that the NH form is stabilized due to intermolecular hydrogen bondings in crystals.

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Supporting Information Available: X-ray crsytallographic data with complete tables of bond lengths, bond angles, and atomic parameters for **1** and **2**, a packing diagram of **2**, electronic spectra of **2**, and details on the estimation of the populations of the OH and NH forms in the crystals of **2** (31 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(10) Theilacker, W.; Kortüm, G.; Friedheim, G. *Chem. Ber*. **1950**, *83*, 508−519.

(11) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. Typical interatomic distances: organic compounds. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; The International Union of Crystallography; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; Vol. C, pp 685−706.

(12) The EPA solution is the mixed solution of ether, isopentane, and ethanol in the volume ratio of 5:5:2.

(13) The distance and angle shows that the intermolecular hydrogen bonding is of medium strength, see: Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997; pp 11−16.

(14) A similar intermolecular O···H−O hydrogen bonding occurs in the crystals of 2-hydroxy-*N*-(2-hydroxybenzylidene)aniline,[15] *N*-(2,3-dihydroxybenzylidene)-2-hydroxymethylaniline,[16] and *N*-(2,3-dihydroxybenzylidene)-isopropylamine.[17] For these compounds the NH form was detected in crystals.

(15) (a) Lindeman, S. V.; Antipin, M. Yu.; Struchkov, Y. T. *Kristallografiya* **1988**, *33*, 365−369. (b) Zheglova, D. K.; Gindin, V.; Kol'tsov, A. I. *J. Chem. Res., Synop.* **1995**, 32−33.

(16) Puranik, V. G.; Tavale, S. S.; Kumbhar, A. S.; Yerande, R. G.; Padhye, S. B.; Butcher, R. J. *J. Crystallogr. Spectrosc. Res.* **1992**, *22*, 725−730.

(17) Mansilla-Koblavi, F.; Tenon, J. A.; Ebby, T. N.; Lapasset, J.; Carles, M. *Acta Crystallogr. Sect. C* **1995**, *51*, 1595−1602.