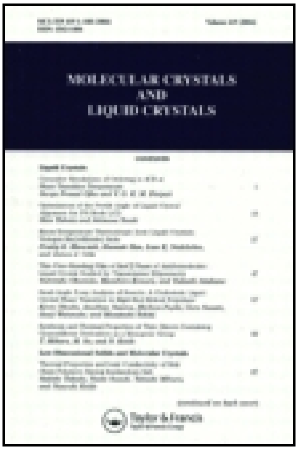


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Crystallographic Study on the Thermochromism of Salicylideneanilines

Keiichiro Ogawa [a], Toshikatsu Fujiwara [a] & Jun Harada [a]

[a] Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo, 153-8902, Japan

To cite this article: Keiichiro Ogawa, Toshikatsu Fujiwara & Jun Harada (2000): A Crystallographic Study on the Thermochromism of Salicylideneanilines, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 344:1, 169-178

To link to this article: http://dx.doi.org/10.1080/10587250008023832

Mol. Cryst. Liq. Cryst., 2000, Vol. 344, pp. 169-178
Reprints available directly from the publisher
Photocopying permitted by license only

A Crystallographic Study on the Thermochromism of Salicylideneanilines

KEIICHIRO OGAWA*, TOSHIKATSU FUJIWARA and JUN HARADA

Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153–8902, Japan

A variable temperature X-ray crystallographic analysis of *N*-(5-chloro-2-hydroxybenzylidene)-4-hydroxyaniline showed the crystal structure change associated with the thermochromism.

Keywords: Salicylideneaniline; Thermochromism; Tautomerization; Intermolecular hydrogen bonding

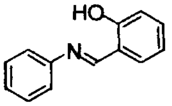
INTRODUCTION

Salicylideneanilines belong to a class of most popular compounds which show thermochromism and photochromism in crystals.[1] They usually exist as crystalline materials with colors ranging from pale

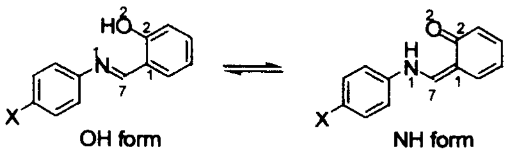
---

* E-mail: ogawa@ramie.c.u-tokyo.ac.jp

yellow through orange to deep red at room temperature. For example, the parent compound (**1**) is pale yellow at room temperature in crystals. It does not change in color with variation of the temperature, whereas it becomes red when it is irradiated with ultraviolet light.[2] In contrast, the crystals of a chloro derivative *N*-(5-choloro-2-hydroxybenzylidene)aniline (**2**) are thermochromic. The crystals of **2** are orange-red at room temperature and become pale yellow when they are cooled to 77 K. The color change is reversible. Thus, the chromic behavior of the crystals of salicylideneanilines is different from compound to compound. Furthermore, the behavior strongly depends on the crystal structure. For example, in the case of *N*-salicylidene-2-methylaniline, the crystals obtained from methanol are photochromic, whereas the crystals from petroleum-ether are thermochromic. [2]



1



(1)

2: X=H **3**: X=OH

The thermochromism of crystalline salicylideneanilines is ascribed to the tautomerism between the OH and NH forms (eq 1). In most cases, the OH form is more stable than the NH form. With raising the temperature, the population of the less stable NH is increased. For example, in the electronic spectrum of crystalline **2**, the absorption band at ca. 470 nm, which is assigned to the NH form, increases in intensity with the raising the temperature. Although X-ray crystallgraphic analyses of **2** at different temperature were carried out, no significant change was observed for the crystal structure with variation of the temperature. A change in the crystal structure associated with the thermochromism of salicylideneanilines has never been observed.[3] This paper reports the observation of the crystal structure change for the thermochromism of salicylideneanilines, using variable temperature X-ray analysis of *N*-(5-chloro-2-hydroxy-benzylidene)-4-hydroxyaniline (**3**).[4]

RESULTS AND DISCUSSION

Perspective views of the molecule of **3** are shown in FIGURE 1. Selected bond lengths obtained from the X-ray crystallographic analyses of **3**[5] are listed in TABLE 1. Bond lengths of **2**,[6] which are regarded as of the pure OH form,[7] are also listed in TABLE 1 for comparison.

TABLE 1. Selected bond lengths of **2** and **3** (Å)

compd	*T* (K)	O2–C2	C2–C1	C1–C7	C7–N1
2	90	1.350(2)	1.412(3)	1.457(3)	1.291(2)
3	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)

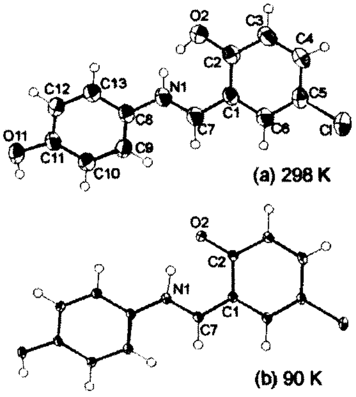


FIGURE 1. Perspective view of **3** with the atom numbering scheme: (a) at 298 K and (b) at 90 K. The ellipsoids are drawn at the 50 % probability level.

TABLE 1 shows that the each length of the bonds which could change in bond order by the tautomerism is significantly different between **2** and **3**. Thus, O2–C2 bond of **3** is shorter than that of **2** and C1–C7 bond of **3** is also shorter than that of **2**; C2–C1 bond of **3** is longer than that of **2** and C7–N1 bond of **3** is also longer than that of **2**. The results suggest that the NH form might coexist in the crystals of **3**.

The most important point is that lengths of these bonds of **3** systematically vary with the temperature. Thus, the lengths of 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 whereas the structure at 90 K was refined as the pure NH form. Thus, the X-ray diffraction unambiguously displayed the occurrence of the tautomerism that favors the NH form in crystals.

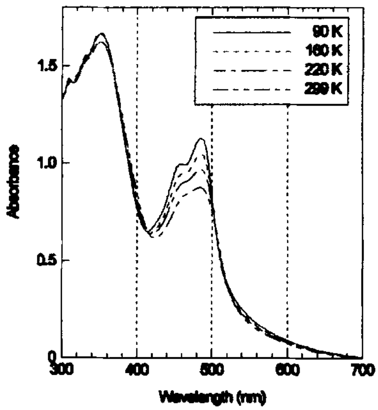


FIGURE 2. Electronic spectra of **3** in a transparent KBr disk.

Electronic spectra show that the crystals of **3** are thermochromic [FIGURE 2]. 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 **3** 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 by the use of the method reported by Theilacker *et al.*[8] 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. The results reveal that ca. 90 % of **3** exists as the NH form in crystals at 90 K and that the energy difference between the NH and OH forms is ca. 0.4 kcal mol^{-1} in crystals.

The color of the crystals of **3** is orange at 298 K and pale yellow at 77 K. The color lightening of the crystal with lowering the temperature apparently contradicts with the change in the electronic spectra, from which a color deepening is expected. The contradiction can explained if the increase in the intensity of the fluorescence band at 520 nm with lowering the temperature [FIGURE 3] is taken into account. The increase in the absorption at 485 nm is outweighed by the increase in the emission at a close wavelength. Thereby the color of the crystals changes from orange to yellow with lowering the temperature.

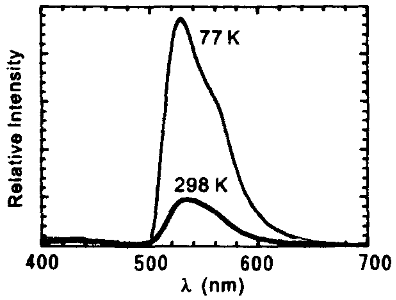
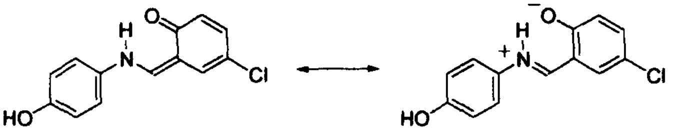


FIGURE 3. Fluorecence spectra of **3** (excited at 365 nm) in a transparent KBr disk.

The geometry of **3** at 90 K is significantly different from that expected for a typical "keto" form **3k**. 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,[9] 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 **3** has the character of the zwitter ion **3ki** considerably.



3k **3ki** (2)

In contrast to the crystalline state, **3** favors the OH form in solution. This was evidenced by electronic spectra. The spectra of the EPA solution[10] 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 **3** 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 **3** reveal the occurrence of the intermolecular hydrogen bonding [FIGURE 4]. 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.[11,12] It is therefore concluded that the stabilization of the NH form in the crystals of **3** results primarily from the intermolecular hydrogen bonding in crystals.

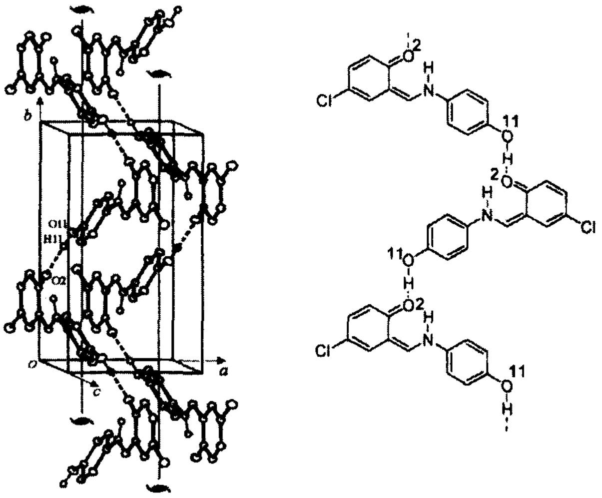


FIGURE 4. Packing diagram of **3** (left) and the intermolecular hydrogen bondings (right).

CONCLUSION

This study evidences the following points: (i) The thermochromism of **3** in crystals is originated from the tautomerism between the OH and NH forms; (ii) The NH form has a character of zwitter ion considerably in crystals; (iii) The NH form is stabilized due to intermolecular hydrogen bondings in crystals; (iv) The apparent color change of the crystals is due to the strong temperature dependence of the fluoresence. This study also demonstrates that the variable temperature X-ray crystallographic analysis is a powerful tool for the study on the thermochromism of organic crystals.

References

[1] Review: (a) E. Hadjoudis, M. Vittorakis, I. Moustakali-Mavridis, *Tetrahedron*, **43,** 1345 (1987). (b) E. Hadjoudis, *Photochromism*, Eds. H. Dürr and H. Bouas-Laurent, Elesevier, Amsterdam, pp. 685 (1990). (c) T. Inabe, *New J. Chem.*, 15, 129 (1991). (d) E. Hadjoudis, *Molecular Engineering*, 3, 301 (1995).

[2] (a) M. D. Cohen, G. M. J. Schmidt, *J. Phys.Chem.*, **66,** 2442 (1962). (b) M. D. Cohen, G. M. J. Schmidt, S. Flavin, *J. Chem. Soc.*, 2041 (1964).

[3] J. Bregman, L. Leriserowitz, G. M. J. Schmidt, *J. Chem. Soc.*, 2068 (1954).

[4] K. Ogawa, Y. Kasahara, Y. Ohtani, J. Harada, *J. Am. Chem. Soc.*, **120,** 7107 (1998).

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

[6] The X-ray structure of **2** was redetermined with higher accuracy in this study. Our structure was essentially identical with that determined by Bregman *et al.*[3] The crystallographic data: $C_{13}H_{10}ClNO$, MW = 231.67, orthorhombic, space group $Pca2_1$, $Z = 4$, $\lambda(\mathrm{Mo, K\alpha}) = 0.71073$ 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.

[7] It was proved by Schmidt and co-workers that **2** exists exclusively as the OH form at 90 K in crystals.[3].

[8] W. Theilacker, G. Kortüm, G. Friedheim, *Chem. Ber.*, **83,** 508 (1950).

[9] F. H. Allen, O. Kennard, O, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *International Tables for Crystallography*, Vol. C. A. J. C. Wilson, Ed. The International Union of Crystallography; Kluwer Academic Publishers: Dordrecht, The Netherlands, pp 685 (1995).

[10] The EPA solution is the mixed solution of ether, isopentane, and ethanol in the volume ratio of 5:5:2.

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

[12] A similar intermolecular O···H-O hydrogen bonding occurs in the crystals of 2-hydroxy-*N*-(2-hydroxybenzylidene)aniline,[13] *N*-(2,3-dihydroxybenzylidene)-2-hydroxymethylaniline,[14] and *N*-(2,3-dihydroxybenzylidene)isopropylamine.[15] For these compounds the NH form was detected in crystals.

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

[14] V. G. Puranik, S. S. Tavale, A. S. Kumbhar, R. G. Yerande, S. B. Padhye, R. J. Butcher, *J. Crystallogr. Spectrosc. Res.,* **22,** 725 (1992).

[15] F. Mansilla-Koblavi, J. A. Tenon, T. N. Ebby, J. Lapasset, M. Carles, *Acta Crystallogr. Sect. C,* **51,** 1595 (1995).