J. Phys. Chem. A **2001,** *105,* 3425−3427

Thermochromism of Salicylideneanilines in Solution: Aggregation-controlled Proton Tautomerization

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Received: October 27, 2000; In Final Form: January 10, 2001

Many salicylideneanilines have been known to exhibit thermochromism in the solid state. In contrast, in the solution, the thermochromism has rarely been observed. This paper reveals that salicylideneanilines are generally thermochromic in the solution of hydrocarbon solvents and that the proton tautomerization, which is the origin of the thermochromism, is controlled by the aggregation of molecules. This is evidenced by the electronic absorption spectra of salicylideneaniline (**1**), *N*-(5-chloro-2-hydroxybenzylidene)aniline (**2**), *N*-(2-hydroxy-4-methoxybenzylidene)aniline (**3**), *N*-(2-hydroxy-5-nitrobenzylidene)aniline (**4**), *N*-(2-hydroxy-5-nitrobenzylidene)-2,6-dimethylaniline (**5**), and *N*-(3,5-di-*tert*-butyl-2-hydroxybenzylidene)aniline (**6**) in isopentane or the mixture of isopentane and methylcyclohexane (volume ratio = 3:1) at different temperatures between 297 and 77 K. They exhibited a remarkable spectral change with lowering temperature, except for **6**. At 297 K the OH form is exclusively populated. When the temperature is lowered, the absorption bands of the OH form decrease in intensity and new bands that are assigned to the NH form emerge. At 77 K, the OH form disappears and the NH form is exclusively populated. The spectra of **6** do not change with lowering of the temperature.

Introduction

Proton tautomerization plays an important role in many fields of chemistry and biochemistry.[1,2] The tautomerization in salicylideneanilines (eq 1) has been the subject of particular interest,

(1)

because it is closely related to thermo- and photochromism.[3−9] Many salicylideneanilines exhibit thermochromism in the solid state and it is ascribed to the population change of the OH and NH forms with variation of the temperature.[5] In contrast, in solution the thermochromism has rarely been observed,[10] probably because the NH form is too unstable to be populated in solution. We wish to report here that salicylideneanilines are *generally* thermochromic in the fluid solution of isopentane or an isopentane/methylcyclohexane mixture and that the proton tautomerization is controlled by the aggregation of the molecules.

Experimental Section

Materials. Salicylideneanilines were prepared according to standard procedures. New compound **5** was characterized as follows: yellow crystals recrystallized from methanol, mp 132−133 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 14.27 (br s, 1H), 8.43 (s, 1H), 8.34 (d, $J = 3$ Hz, 1H), 8.30 (dd, $J = 9$, 3 Hz 1H), 7.13 (d, $J = 8$ Hz, 2H), 7.12 (d, $J = 9$ Hz, 1H), 7.07 (t, $J = 8$ Hz, 1H), 2.22(s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 167.01, 165.36, 146.51, 139.89, 128.59, 128.41, 128.30, 128.28; 125.85, 118.38, 117.60, 77.26, 77.00, 76.75, 18.40; MS(EI) *m*/*z* 270 (M$^+$).

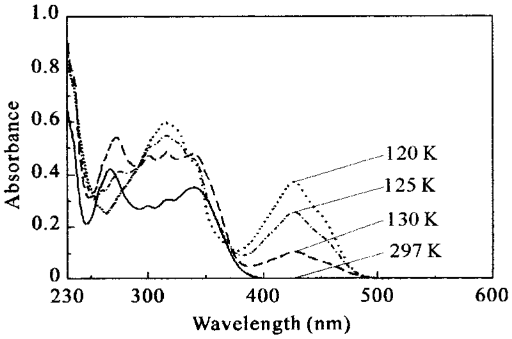

Figure 1. Uncorrected absorption spectra of salicylideneaniline (**1**) in isopentane at different temperatures, 3.6 × 10^{-5} M, path length 1.0 cm.

Measurements. The electronic absorption spectra were measured on a Jasco Ubest50 spectrometer equipped with a liquid nitrogen bath cryostat Oxford DN1704. The temperature of the cryostat was controlled within ±0.1 K. A spectroscopic grade isopentane from Merck (UVASOL) and a spectroscopic grade methylcyclohexane from DOJIN Chemicals (SPECTROSOL) were used as received. Precipitation was not observed for any of the samples. In the determination of the temperature for the appearance of the absorption band that is assigned to the NH form, the emergence of the absorption band was recognized as the deviation of 0.0025 in absorbance from the baseline. The path length of the low concentration solution was 1.0 cm and that of the high concentration solution was 0.1 cm.

Calculations. The molecular geometries for the calculations of the absorption spectra were obtained from the PM3 calculations. The calculations of the spectra were based on the INDO/S-CI method. All the calculations were carried out using the WINMOPAC3 package (2000, FUJITSU, Tokyo, Japan).

Results and Discussion

We measured electronic absorption spectra of salicylideneanilines **1**−**6** in isopentane or the mixture of isopentane and

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10.1021/jp003985f CCC: $20.00 © 2001 American Chemical Society
Published on Web 03/10/2001

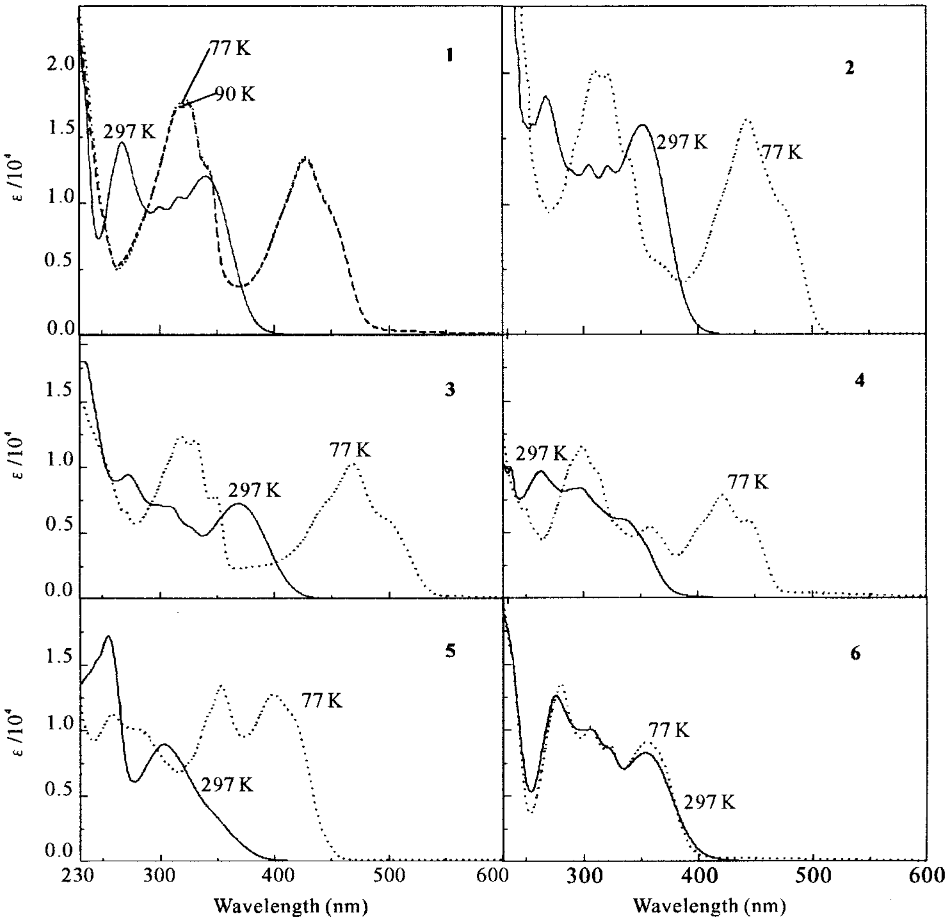
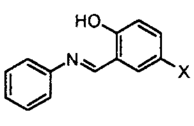
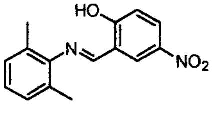


Figure 2. Corrected absorption spectra of salicylideneaniline (**1**), *N*-(5-chloro-2-hydroxybenzylidene)aniline (**2**), *N*-(2-hydroxy-5-methoxybenzylidene)-aniline (**3**), *N*-(2-hydroxy-5-nitrobenzylidene)aniline (**4**), *N*-(2-hydroxy-5-nitrobenzylidne)-2,6-dimethylaniline (**5**), and *N*-(3,5-di-*t*-butyl-2-hydroxy-benzylidene)aniline (**6**) in an isopentane/methylcyclohexane mixture (3:1) at different temperatures at path length 1.0 cm: **1**, 3.4 × 10^{-5} M; **2**, 3.5 × 10^{-5} M; **3**, 4.0 × 10^{-5} M; **4**, 2.2 × 10^{-5} M; **5**, 4.1 × 10^{-5} M; **6**, 4.6 × 10^{-5} M.

methylcyclohexane (volume ratio = 3:1) at different temperatures and found that all the compounds except **6** exhibit a remarkable spectral change with lowering the temperature.



1: X=H, **2**: X=Cl
3: X=OMe, **4**: X=NO₂



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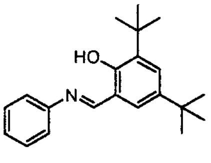

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The absorption spectra of salicylideneaniline (**1**) in isopentane are shown in Figure 1. At 297 K, **1** exhibits only the absorption bands ($\lambda_{\max}$ = 338, 317, 300, and 270 nm) that are assigned to the OH form.[11,12] When the temperature was lowered, the spectrum remarkably changed. From 140 to 115 K (above the melting point of 113.3 K),[13] the absorption bands of the OH form decreased in intensity and new bands with the absorption maxima at 426 and 313 nm emerged. The new bands are assigned to the NH form on the basis of the INDO/S-CI calculations. The spectral change was reversible.

The spectral change indicates that the tautomeric equilibrium markedly shifts to the NH form with lowering of the temperature. Thus, the NH form, which is much less stable than the OH form at room temperature, becomes much more stable at low temperature in the solution.

A similar spectral change was also observed in the isopentane/methylcyclohexane mixture. In this solvent the spectra at lower temperature could be obtained, because the solvent is transparent until 77 K. The spectra for which the solvent contraction effect[14] was corrected did not change in the temperature range between 90 and 77 K (Figure 2a), indicating that the equilibrium shift is completed and the NH form is exclusively populated at 90 K and lower. Herein the first successful observation of the pure NH form of **1** in solution was achieved.

Other salicylideneanilines **2**−**5** also show a similar spectral change in isopentane or the isopentane/methylcyclohexane mixture (Figure 2). The electronic properties of these compounds are considerably different because of the variety of the substituents. The conformation of **5**, in which the N−Ar bond should be severely twisted due to the steric congestion by two methyl groups on the aniline ring, must be distinctly different from that of others. Nevertheless, all the compounds exhibit a similar spectral change with lowering of the temperature. Thus, in isopentane or the isopentane/methylcyclohexane mixture, salicylideneanilines generally undergo the complete shift from the OH form to the NH form with lowering of the temperature.

The results suggest that salicylideneanilines aggregate at low temperature in these solvents and that the NH form is greatly stabilized in the aggregate.

The aggregation is evidenced as follows.

First, the temperature for the appearance of the absorption band that is assigned to the NH form depends on the concentration of the solution (Figure 3). The absorption band at 426 nm emerges at 139 K in the solution of low concentration (3.7 × 10^{-5} M) and emerges at 146 K in the solution of high

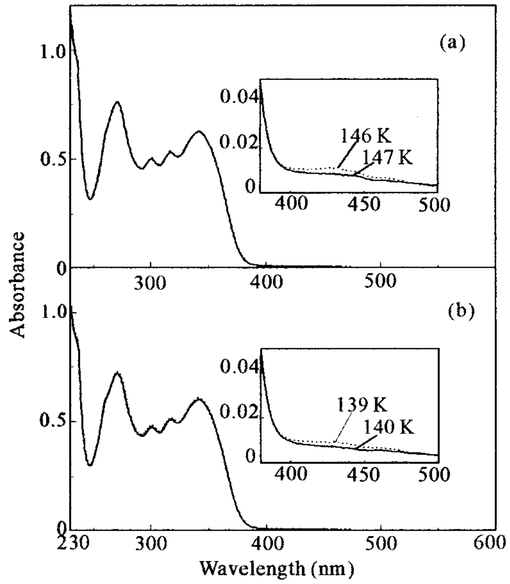


Figure 3. Absorption spectra of salicylideneaniline (**1**) in isopentane of different concentrations at the temperatures where the NH form appears. Inset: Enlargement of the region for the absorption band assigned to the NH form. (a) 3.7 × 10^{-4} M, path length 0.1 cm. Solid and dotted lines represent the spectrum at 147 K and 146 K, respectively. (b) 3.7 × 10^{-5} M, path length 1.0 cm. Solid line 140 K; dotted line 139 K.

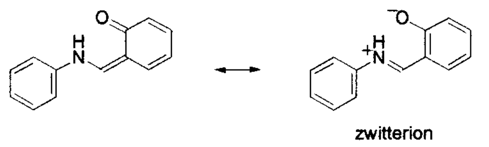
concentration (3.7 × 10^{-4} M). Thus, the NH form appears at higher temperature in the solution of higher concentration.

Second, the spectra of **6**, which has two *tert*-butyl groups, remain unchanged with lowering of the temperature, indicating that **6** exists exclusively as the OH form between 297 and 77 K. The results suggest that the aggregation of **6** is prohibited due to the bulkiness of *tert*-butyl groups on the benzene ring.

Third, the EPA solution of **1** does not exhibit the spectral change with lowering of the temperature.[15] This indicates the interference with the aggregation by ethanol, which forms intermolecular hydrogen bonding with **1**.

The stabilization of the NH form in the aggregate is remarkable. According to the quantum mechanical calculations, the NH form is less stable than the OH form by 4.6 kcal mol^{-1} for a free molecule of **1**.[7] If this energy difference holds in the solution at 77 K, the population of the NH form should be only 10^{-14}. However, in fact, the NH form is exclusively populated, indicating the reversal of the relative stability between the two forms by the aggregation. Thus, the stabilization energy of the NH form in the aggregate would amount, at least, to ca. 5 kcal mol^{-1}.

What is the origin of such a big stabilization of the NH form in the aggregate? We have previously shown that the NH form is predominantly zwitterionic in crystals (eq 2) and is considerably stabilized by electrostatic intermolecular interactions.[6,8] It is therefore most likely that the NH form in the aggregate is also zwitterionic and highly stabilized as in crystals, because a crystal is a kind of aggregate. Thus, the big stabilization of the NH form in the aggregate is ascribed to the zwitterionic character of the NH form.



(2)

Conclusion

We demonstrate in this paper that salicylideneanilines are generally thermochromic in the fluid solution of isopentane or the isopentane/methylcyclohexane mixture and that the proton tautomerization, which is the origin of the thermochromism, is controlled by the aggregation of molecules.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

(1) Reviews: (a) Lehn, J.-M. In *Supramolecular Chemistry*; VCH: Weinheim, 1995. (b) Sugawara, T.; Takasu, I. *Adv. Phys. Org. Chem.* **1999**, *32*, 219−265.

(2) (a) Eichen, Y.; Lehn, J.-M.; Scherl, M.; Haarer, D.; Fischer, J.; DeCian, A.; Corval, A.; Trommsdorff, H. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2530−2533. (b) Goodman, M. F. *Nature* **1995**, *378*, 237−238. (c) Douhal, A.; Kim, S. K.; Zewail, A. H. *Nature* **1995**, *378*, 260−263. (d) Rodríguez-Santiago, L.; Sodupe, M.; Oliva, A.; Bertran, J. *J. Am. Chem. Soc.* **1999**, *121*, 8882−8890. (e) Marcinek, A.; Adamus, J.; Huben, K.; Gebicki, J.; Bartczak, T. J.; Bednarek, P.; Bally, T. *J. Am. Chem. Soc.* **2000**, *122*, 437−443.

(3) Reviews: (a) Inabe, T. *New. J. Chem.* **1991**, *15*, 129−136. (b) Hadjoudis, E. *Molecular Eng.* **1995**, *5*, 301−337. (c) Samat, A.; Lokshin, V. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Kluwer Academic: New York, 1999; Vol. 2, Chapter. 10.

(4) Cohen, M. D.; Schmidt, G. M. *J. Phys. Chem.* **1962**, *66*, 2442−2445.

(5) (a) Dudek, G. O.; Dudek, E. P. *J. Am. Chem. Soc.* **1966**, *88*, 2407−2412. (b) Hadjoudis, E.; Milia, F.; Seliger, J.; Blinc, R.; Zagar, V. *Chem. Phys.* **1980**, *47*, 105−109. (c) 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. (d) Wozniak, K.; He, H.; Klinowski, J.; Jones, W.; Dziembowska, T.; Grech, E. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 77−85. (e) Katritzky, A. R.; Ghiviriga, I.; Leeming, P.; Soti, F. *Magn. Reson. Chem.* **1996**, *34*, 518−526. (f) Alarcón, S. H.; Olivieri, A. C.; Nordon, A.; Harris, R. K. *J. Chem. Soc., Perkin 2* **1996**, 2293−2296. (g) Sekikawa, T.; Kobayashi, T.; Inabe, T. *J. Phys. Chem. A.* **1997**, *101*, 644−649. (h) Alarcón, S. H.; Pagani, D.; Bacigalupo, J.; Olivieri, A. C. *J. Mol. Struct.* **1999**, *475*, 233−240. (i) Pizzala, H.; Carles, M.; Stone, W. E. E.; Thevand, A. *J. Chem. Soc., Perkin 2*, **2000**, 935−939.

(6) Ogawa, K.; Kasahara, Y.; Ohtani, Y.; Harada, J. *J. Am. Chem. Soc.* **1998**, *120*, 7107−7108.

(7) Ogawa, K.; Fujiwara, T. *Chem. Lett.* **1999**, 657−658.

(8) Ogawa, K.; Harada, J.; Tamura, I.; Noda, Y. *Chem. Lett.* **2000**, 528−529.

(9) Harada, J.; Uekusa, H.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 5809−5810.

(10) The absorption spectra of the following salicylideneanilines in hydrocarbon solvents were reported to *exceptionally* undergo a pronounced change with lowering of the temperature and it was assigned to the increase in the population of the NH form. *N*-Salicylidene-3-methylaniline: (a) Cohen, M. D.; Hirshberg, Y.; Schmidt, J. M. *J. Chem. Soc.* **1964**, 2051−2059. (b) Cohen, M. D.; Flavian, S. *J. Chem. Soc. (B)* **1967**, 317−321. *N*-(2-Hydroxy-3-nitrobenzylidene)aniline, *N*-(2-hydroxy-5-nitrobenzylidene)aniline (**2**), and *N*-(2-hydroxy-5-nitrobenzylidene)-2,4-dimethylaniline: (c) Becker, R. S.; Richey, W. F. *J. Am. Chem. Soc.* **1967**, *89*, 1298−1302. A similar spectral change was also reported for salicylidenebenzylamines: (d) Lambi, E.; Gegiou, D.; Hadjoudis, E. *J. Photochem. Photobiol. A* **1995**, *86*, 241−246.

(11) Ottolenghi, M.; McClure, S. D. *J. Chem. Phys.* **1967**, *46*, 4613−4620.

(12) Dudek, G. O.; Dudek, E. P. *J. Am. Chem. Soc.* **1966**, *88*, 2407−2412.

(13) Mulov, S. L. *Handbook of Photochemistry*; Mercel Dekker: New York, 1973; p 86.

(14) Passerini, R.; Ross, I. *J. Sci. Instrum.* **1953**, *30*, 274−276.

(15) See ref 11. The EPA solution is the mixed solution of ether, isopentane, and ethanol in the volume ratio of 5: 5: 2.