Observation of Thermal Tautomerism of Thermochromic Salicylideneaniline Derivatives in the Solid State by ^{15}N CPMAS NMR down to Cryogenic Temperatures

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The temperature dependent solid state ^{15}N CPMAS NMR spectra of ^{15}N enriched salicylideneaniline derivatives, *N*-salicylideneaniline (SA), N,N′-bissalicylidene-p-phenylenediamine (BSP) and N,N′-di(2-hydroxy-1-naphthylidene)-p-phenylenediamine (DNP) were measured in order to study possible proton transfer processes in the NHO hydrogen bonds. For DNP a remarkable change of the ^{15}N chemical shifts of more than 50 ppm was observed between 26 and 388 K by using the CPMAS NMR technique down to cryogenic temperatures. The result clearly indicates very small enthalpy differences among the four tautormers associated with the combination of two possible forms, OH and NH form, of the two NHO hydrogen bonds in a DNP molecule.

1. Introduction

High resolution ^{15}N solid state NMR under conditions of cross polarization (CP), magic angle spinning (MAS) and proton decoupling is a sensitive tool for the characterization of proton transfer in N···H···X hydrogen bonded systems [1–9]. In the second and millisecond time scale the proton transfer can be detected by magnetization transfer techniques [1] and line shape analysis [2–4]. In the micro- to nanosecond time scale rates of proton transfer can be obtained by analysis of the longitudinal ^{15}N T_1 relaxation times [5] which complements the well established technique of T_1 measurements by wide line ^{1}H NMR [10]. The latter has advantages, such as good signal to noise ratio for for most organic compound and capability to perform measurements in a very wide temperature range, particularly at very low temperature. By contrast, CPMAS NMR experiments are usually very difficult below 100 K. On the other hand, the advantage of high resolution ^{15}N CPMAS NMR is that the dependence of ^{15}N shifts on temperature provides detailed information about equilibrium constants K and reaction enthalpies of solid state transfer from and to nitrogen [1–9]. These quantities are very useful for minimizing the number of parameters needed for the analysis of the relaxation times revealing the rate constants and the mechanism of the proton transfer, classical or quantal [10].

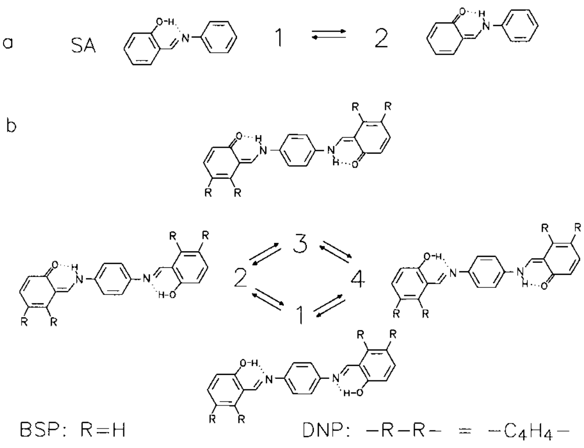

Fig. 1
Structure and reaction scheme of SA, BSP and DNP

In this paper, variable temperature ^{15}N CPMAS NMR was employed to detect possible proton transfer processes in salicylideneaniline derivatives (Fig. 1). The latter had been invoked in order to explain the thermochromism and photochromism of this class of compounds [11–13]. This phenomenon might be used in the future for the development of optical materials for molecular technology. However, to our knowledge, thermal equilibrium constants of the tautomeric process have not yet been directly determined as it is difficult to estimate the extinction coefficients of the different forms by UV/Vis-spectroscopy. For *N*-salicylidenenaniline (SA) two tautomeric states may be formed interconverting by proton transfer in the NHO hydrogen bond (Fig. 1 a). Evidence for the formation of four tautomeric states based on the proton transfer motion in two coupled NHO hydrogen bonds (Fig. 1 b) has been obtained by one of the authors for the cases of N,N′-bissalicylidene-p-phenylenediamine (BSP) and N,N′-di(2-hydroxy-1-naphthylidene)-p-phenylenediamine (DNP) from the analysis of the longitudinal ^{1}H NMR relaxation times of the polycrystalline specimens [10, 14]. This analysis is based on a theory of longitudinal dipolar ^{1}H relaxation caused by stepwise double proton transfer involving four non-equivalent tautomeric states. Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at the N K- and O K-edges and X-ray photoelectron spectroscopy (XPS) of BSP and DNP in the N1s and O1s regions also

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indicated the existence of both OH and NH forms of the NHO hydrogen bonds [15]. These results incited us to try to measure the equilibrium constants of the tautomeric processes in solid BSP and DNP by ^{15}N CPMAS NMR of the ^{15}N labeled analogs. This method has been applied by some of us in the case of tetramethyltetraaza(14)annulene (TTAA) [2, 7, 8] which also contains two protons rapidly exchanging among four inequivalent tautomeric states. The ^{1}H T_1 measurement of polycrystalline DNP strongly indicated that the energy differences among the tautomers are very small [10, 14]. Thus, the measurement of ^{15}N CPMAS NMR had to be extended to the very low temperature region (ca. 25 K). This problem could be solved using a cryogenic CPMAS NMR probe. In the following, we firstly describe the experimental details and the formalism for obtaining equilibrium constants of four-site proton transfer by ^{15}N chemical shift analysis. Then, the results obtained for SA, BSP and DNP are reported and discussed.

2. Experimental

2.1 Materials

^{15}N labeled salicylideneaniline, doubly ^{15}N labeled BSP and DNP were prepared by condensation of ^{15}N-aniline or of ^{15}N$_2$-p-phenylenediamine with salicylaldehyde and 2-hydroxy-1-naphthylaldehyde, respectively [16]. The preparation of ^{15}N$_2$-p-phenylenediamine was carried out along the method analogous to the previously reported one for ^{15}N$_2$-o-phenylenediamine [6].

2.2 NMR-Measurements

In Berlin, the ^{15}N CPMAS NMR measurements were performed between 130 and 400 K at 9.12 MHz (2.1 T cryomagnet) using a Bruker CXP 100 NMR spectrometer equipped with a 7 mm Doty CP/MAS probe (DSI-163). For the low temperature measurements, nitrogen gas was used as bearing and driving gas and cooled by using a home built-heat exchanger [17]. Control of the temperature was achieved with a Bruker BVT-1000, a 4 Ω heater and a copper-constantane thermocouple. The temperature of the specimen was determined with a calibrated Degussa Pt-100-thermometer.

For the measurement of the ^{15}N chemical shifts of DNP at cryogenic temperatures we employed a Bruker DSX 400 spectrometer equipped with a cryogenic-temperature CPMAS NMR probe (Doty Penguin probe) at the Institute for Molecular Science (IMS), Okazaki, Japan. Sample spinning of more than 2 kHz was achieved at 26 K. Unfortunately, the NMR lines of all sample measured with the Penguin probe showed an artifical low field shift contribution which we attribute to some material used for constructing the probe. Thus, the chemical shift data had to be corrected in the low temperature region. The low field shift was calibrated by using the shift of ^{79}Br spectrum of pulverized KBr obtained under the same experimental conditions as those used for DNP. The observed chemical shift of ^{79}Br could be described by the function $\delta(^{79}\mathrm{Br}) = 10.73 + 439.9/T - 6.07\times10^{-2}\times T + 7.09\times10^{-5}\times T^2$ ppm. $\delta(^{79}\mathrm{Br})$ was set to 0 ppm at 306 K and T is the absolute temperature. The second term +439.9/T ppm, which dominates at very low temperature, is unexpected for a diamagnetic KBr sample and was, therefore, substracted from the raw ^{15}N chemical shifts of DNP (in the ppm scale). All chemical shift values were referenced to external solid ^{15}NH$_4$Cl (95% ^{15}N enriched).

3. Theoretical Section

In this section we describe a model of the temperature dependence of ^{15}N NMR chemical shifts for double proton transfers in a system with two coupled NHO hydrogen bonds.

The four tautomeric states i = **1** to **4** shown in Fig. 1 are characterized by the mole fractions x_i. Two nitrogen atoms N$_A$ and N$_B$ in a molecule are characterized by the intrinsic ^{15}N chemical shifts $\delta_i(\mathrm{N_A})$ and $\delta_i(\mathrm{N_B})$. In the region of fast exchange between the four tautomeric states, the averaged ^{15}N chemical shifts δ of an individual nitrogen nucleus N$_A$ or N$_B$ is given by

$$\delta = x_1\delta_1 + x_2\delta_2 + x_3\delta_3 + x_4\delta_4\ . \tag{1}$$

The equilibrium constants are given by the van't Hoff equation,

$$K_{ij} = x_j/x_i = \exp\left(-\frac{\Delta G_{ij}}{RT}\right) = \exp\left(\frac{\Delta S_{ij}}{R} - \frac{\Delta H_{ij}}{RT}\right)\ , \tag{2}$$

where ΔG_{ij} is the free reaction enthalpy, R the gas constant, T the absolute temperature, ΔS_{ij} the reaction entropy and ΔH_{ij} the reaction enthalpy. Assuming that the intrinsic ^{15}N chemical shifts of BSP and DNP only depend on whether the nitrogen atoms are protonated or not, i.e. on δ_{NH} and δ_{N}, it follows that

$$\delta^{\mathrm{A}} = (x_1 + x_4)\delta_{\mathrm{N}} + (x_2 + x_3)\delta_{\mathrm{NH}} \tag{3}$$

and

$$\delta^{\mathrm{B}} = (x_1 + x_2)\delta_{\mathrm{N}} + (x_3 + x_4)\delta_{\mathrm{NH}}\ . \tag{3}$$

Two of the four tautomers, **2** and **4** in Fig. 1b, may exhibit similar free energies in the solid state, since a crystallographic inversion symmetry exists at the center of the molecule both for BSP and DNP [14, 16]. Therefore, we assume that the two nitrogen atoms in a given molecule are equivalent, i.e. also the two tautomers **2** and **4**. In this case, $x_2 = x_4$ and it follows that

$$\delta \equiv \delta^{\mathrm{A}} = \delta^{\mathrm{B}} = (x_1 + x_2)\delta_{\mathrm{N}} + (x_2 + x_3)\delta_{\mathrm{NH}}\ . \tag{5}$$

Using the identity $x_1 + x_2 + x_3 + x_4 = x_1 + 2x_2 + x_3 = 1$, it follows by simple arithmetic that

$$\delta = \delta_{\mathrm{N}} + (x_2 + x_3)(\delta_{\mathrm{NH}} - \delta_{\mathrm{N}}) \, . \tag{6}$$

Inserting the equilibrium constants expressed by Eq. (2) into Eq. (6), we obtain

$$\delta = \delta_{\mathrm{N}} + \frac{K_{12}(1+K_{23})}{1+K_{12}(2+K_{23})}(\delta_{\mathrm{NH}} - \delta_{\mathrm{N}}) \, . \tag{7}$$

For the discussion of the measured temperature dependence of the chemical shift associated with the proton transfer in the NHO hydrogen bonds, we assume that $\Delta S_{\mathrm{ij}} \approx 0$ as usual for intramolecular proton transfers [1–9] and that the instrinsic chemical shifts, δ_{NH} and δ_{N}, are temperature independent. In this case, δ only depends on the four parameters ΔH_{12}, ΔH_{23}, δ_{NH} and δ_{N}.

4. Results and Discussion

Fig. 2 shows a collection of variable temperature ^{15}N CPMAS spectra of SA, BSP and DNP. In each case only one signal was observed. The line width of SA is the largest one, which could suggest the presence of slightly different molecules in the asymmetric unit or some amorphous components. The signal position of SA is temperature independent and located at 257 ppm which is typical for non-protonated sp^2-nitrogen atoms [1–9, 18, 19]. Therefore, for SA only the OH form can be detected using this method.

For BSP which is known to be thermochromic [16], a chemical shift of 234 ppm is observed at room temperature. A possible dependence of this value as a function of temperature could not be detected within the poor spectral resolution of ca. 10 ppm as shown in Fig. 2 b. The reaction enthalpies ΔH_{12} and ΔH_{23} were estimated by analysis of the longitudinal relaxation time T_1 of proton NMR, supposing the exchange processes among the four tautomers shown in Fig. 1b [10]. The estimated values ΔH_{12} = 4 kJ/mol and ΔH_{23} = 8.5 kJ/mol predict chemical shift changes of almost 15 ppm in the temperature region between 163 and 320 K, assuming intrinsic values δ_{NH} = 110 ppm and δ_{N} = 240 ppm for BSP. The estimate of ΔH_{12} from the T_1 of ^{1}H NMR slightly depends on the assignment of the unknown relaxation process in the lowest temperature region [10]. Some refinement of the model used for the analysis of proton relaxation time may be required. For example, a direct exchange process between quasi-degenerate tautomers **2** and **4** could reduce the ^{1}H T_1 values while this process does not affect the temperature dependence of the ^{15}N chemical shift.

In contrast to BSP, the ^{15}N signal of DNP is sharp and appeares at 183 ppm at room temperature. The remarkably high field shifted strongly indicates an enhanced formation of the NH tautomers **2**, **3**, and **4**, even at room temperature, as compared to BSP. The peak strongly shifts downfield when the temperature is decreased as depicted in Fig. 2 c. The chemical shift values at different temperatures are listed in Table 1 including the values measured using the cryogenic temperature CPMAS probe between 26 and 306 K. The shift values obtained with this probe were corrected as discussed in the experimental section. The thermometer of the cryogenic temperature CPMAS probe was not calibrated by any reference sample, since there exists no appropriate reference material to our knowledge. The plot of all data showed a good overlap between the values measured using the cryogenic temperature CPMAS probe at IMS Japan and those obtained in Berlin, as shown in Fig. 3.

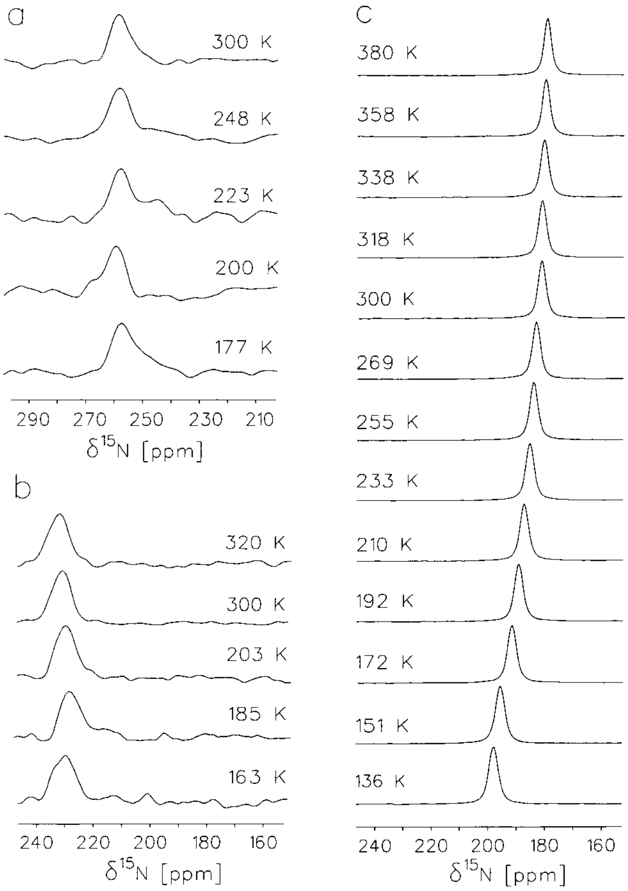

Fig. 2
Variable temperature ^{15}N-CP/MAS NMR spectra of (a) SA, (b) BSP and (c) DNP measured at 9.12 MHz with 2 kHz spinning speed, 9 µs 90° pulses, 4 ms CP time, and 1000 scans on average. The chemical shift was measured from the external reference of pulverized ^{15}NH$_4$Cl (δ(^{15}NH$_4$Cl) = 0 ppm). The chemical shift of ^{15}NH$_4$Cl is located at –353 ppm from liquid nitromethane [18, 19]

The equilibrium constants K_{12} and K_{23} were estimated by least-squares fitting of theexperimental data to Eq. (7). A free data fit did not lead to a unique set for the four parameters. However, as indicated in Fig. 3, the corrected chemical shift seems to converge at about 235 ppm in the low temperature limit. Supposing that this value corresponds to the intrinsic chemical shift δ_{N} of the non-protonated nitrogen atom, a good fit was obtained as shown by solid curve in Fig. 3 with the values ΔH_{12} = 1.4 kJ/mol, ΔH_{23} = 0.2 kJ/mol and a chemical shift of the protonated nitrogen atoms δ_{NH} = 107 ppm. The enthalpy differences among the tautomers of DNP are very small in spite of

Table 1
^{15}N chemical shifts of polycrystalline DNP as a function of temperature

T/K	δ/ppm	*T*/K	δ/ppm	*T*/K	δ/ppm	*T*/K	δ/ppm
26	233.1[a])	100	208.9[a])	183	191.3[b])	295	183.3[b])
30.5	232.1[a])	125	201.1[a])	192	190.2[b])	300	183.2[b])
39	231.8[a])	125	199.3[a])	200	188.3[a])	306	182.5[a])
39.4	232.5[a])	136	199.3[b])	200	188.1[a])	309	182.7[b])
40	232.1[a])	145	197.7[b])	200	189.7[b])	318	182.2[b])
50	229.5[a])	150	195.4[a])	210	188.6[b])	328	182.2[b])
57	226.1[a])	150	194.5[a])	224	186.3[a])	338	181.6[b])
57.5	227.3[a])	151	196.6[b])	225	187.0[b])	347	181.6[b])
69	221.0[a])	158	195.5[b])	233	186.5[b])	358	181.1[b])
78.5	217.1[a])	172	192.9[b])	249	184.4[a])	369	181.1[b])
80	215.3[a])	175	190.6[a])	250	185.2[a])	380	180.6[b])
99	207.3[a])	175	191.4[a])	255	185.4[b])	388	180.6[b])
99	209.3[a])	175	191.7[a])	269	184.3[b])		

[a]) Data measured at IMS, Japan (see in text of experimental section).
[b]) Data obtained in Berlin, Germany.

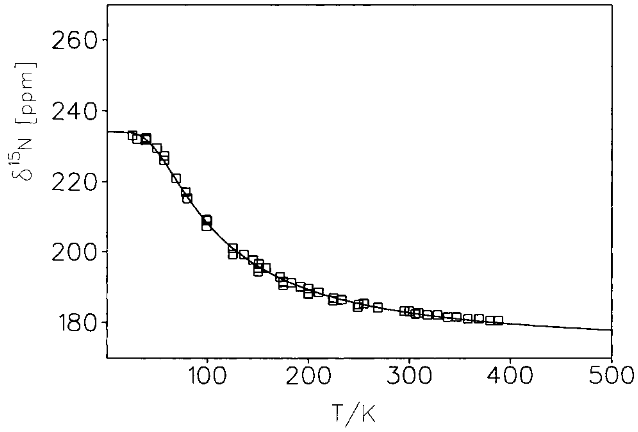

Fig. 3
^{15}N chemical shift of DNP as a function of temperature. Solid line was calculated using Eq. (7). The chemical shift of nonprotonated nitrogen atom was fixed to the value of $\delta_N = 235$ ppm and other parameters $\Delta H_{12} = 1.4$ kJ/mol, $\Delta H_{23} = 0.2$ kJ/mol and $\delta_{NH} = 107$ ppm were obtained by non-linear least-squared fitting

the fact that the tautomerism is associated with the proton transfer in chemically asymmetric NHO hydrogen bonds. This is a remarkable property of DNP. A similar result was obtained from the analysis of the proton relaxation time T_1 together with an evidence of proton tunneling in the NHO hydrogen bonds [10, 14].

5. Conclusions

We have shown that ^{15}N CPMAS NMR was able to detect a solid state proton tautomerism of DNP as postulated by Takeda et al. [10, 14]. Moreover, only one line was observed for DNP, indicating the energetic equivalence of the two tautomeric forms **2** and **4** in Fig. 1. In the case of BSP, the present ^{15}N NMR method is not sensitive enough to detect potential tautomeric states as the lower detection limit is of the order of a few percent.

^{15}N chemcial shift analysis of DNP in a very wide temperature region down to 26 K with cryogenic ^{15}N CPMAS NMR leads to a crude estimate of the enthalpy differences between the tautomeric states **2** and **1**, and between **3** and **2** depicted in Fig. 1. We note that the knowledge of the accurate enthalpy difference values enables us to describe the precise temperature dependence of the ^{15}N chemical shifts of DNP. Thus, DNP could be used as a temperature standard for cryogenic ^{15}N CPMAS NMR in the future.

In addition, we are planning two sets of experiments. One set involves ^{15}N NMR experiments based on the temperature dependent dipolar ^{15}N-D coupling [9] for obtaining further information about the proton and deuteron positions in the hydrogen bonds of salicylideneaniline derivatives. The other one involves ^{15}N T_1 measurements which complement the ^{1}H relaxation experiment [20].

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