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Tautomeric structure of *N*-salicylideneaniline derivatives studied by soft X-ray absorption spectroscopy and X-ray photoelectron spectroscopy

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The tautomeric structures in solid phase were studied by near-edge X-ray absorption fine structure (NEXAFS) and X-ray photoelectron spectroscopy (XPS) for five *N*-salicylideneaniline derivatives. The observed features in the NEXAFS spectra were assigned by (1) the comparison with the core excitation spectra of reference compounds and (2) ab initio MO calculations of the core-excited states by the improved virtual orbital method. The relative intensity of the observed peaks characteristic of each tautomer enabled us to deduce the tautomeric structures of these compounds. The XPS spectra allowed quantitative estimation of the relative tautomer populations. These structures are consistent with the previous estimation by X-ray diffraction. These results demonstrate the usefulness of NEXAFS as well as XPS for studying the tautomerism in hydrogen bonded systems.

Keywords : NEXAFS, XPS, Tautomerism, Hydrogen Bond,

1. Introduction

It is known that some *N*-salicylideneaniline (SA) derivatives show tautomerism in solid state by moving the proton through an intramolecular hydrogen (H-) bond, as shown in Figure 1. The control of this protonic motion is expected to be a unique feature with possible application to electronic devices, since such proton transfer causes the change in the π-electron system (Inabe 1991). For using such compounds as electronically functional materials, Inabe and co-workers studied the H-bonded structure of various SA derivatives by X-ray diffraction (XD) and infrared absorption (IR) spectroscopy and concluded that the electronic and the protonic states are actually strongly coupled (Inabe 1991). However, ambiguity still remains even about the structure. Thus studies by other reliable method have been desired.

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy is a recently developed method, which offers information about chemical bonding around the excited atom (Stöhr 1992). So far no NEXAFS study of such tautomerism has been made, and it will be valuable to examine how this phenomenon appears in NEXAFS and whether NEXAFS can be used for studying the tautomerism.

X-ray photoelectron spectroscopy (XPS) is another useful method for clarifying the chemical structure. Binding energies of the spectral features are sensitive to the chemical environment of the ionized atom, and it may be possible to distinguish the tautomers in SA derivatives.

In this work, we report a combined study of five SA derivatives by NEXAFS and XPS spectroscopies. The analyses of the NEXAFS spectra provided a rather clear picture about the tautomeric structures, demonstrating the usefulness of NEXAFS for investigating the tautomerism. The relative population of the OH- and NH-forms could be also deduced from the XPS spectra.

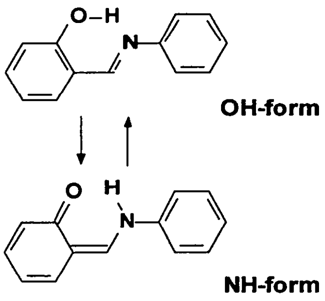

Figure 1

Tautomerism in *N*-salicylideneaniline.

2. Experimental Section

Five *N*-salicylideneaniline derivatives in Figure 2 were used. They are *N,N'*-disalicylidene-1,6-pyrenediamine (DSPY), *N,N'*-disalicylidene-*p*-phenylenediamine (BSP), *N*-(2-hydroxy-1-naphthylidene)-1-pyrenylamine (NPY), *N,N'*-di(2-hydroxy-1-naphthylidene)-*p*-phenylenediamine (DNP), and the complex between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and DNP (DNP-TCNQ). The NEXAFS and XPS specimens except for DNP-TCNQ were prepared by vacuum evaporation at 10^{-3} Pa on Cu plates. The film thickness was 100-150 nm as monitored by a quartz oscillator. The sample of DNP-TCNQ was prepared by scrubbing the sample powder on a scratched Ni plate.

N *K*- and O *K*-edge NEXAFS experiments with the total electron yield mode were carried out at the beamline 11A of Photon Factory at National Institute for High Energy Physics (KEK-PF). The energy calibration was carried out taking main peaks of TCNQ at the N *K*-edge and potassium sulfate (K_2SO_4) at the O *K*-edge to be at 399.6 eV and 536.9 eV, respectively (Narioka & Seki 1992).

The ab initio MO calculations with the minimal basis set were performed for a planar SA molecule in the OH- and NH-forms (Figure 1). We used the program GSCF3 coded by one of the authors (N. K.). Calculations for the core-ionized and core-excited states were carried out for the N and O atoms. The excitation energies for the core-excited states were obtained as the term value (ionization energy minus excitation energy). The transition intensities were obtained by calculating the transition dipole moments. From these results, the NEXAFS spectra were simulated as the weighted sum of Gaussian functions at excitation energies.

XPS measurements were carried out on an Escalab 220i spectrometer (Vacuum Generators) using Mg *K*α X-ray source. Peak positions and areas were determined by the curve fitting with the abscissa being determined by assuming the C1s main peak to be at 284.0 eV.

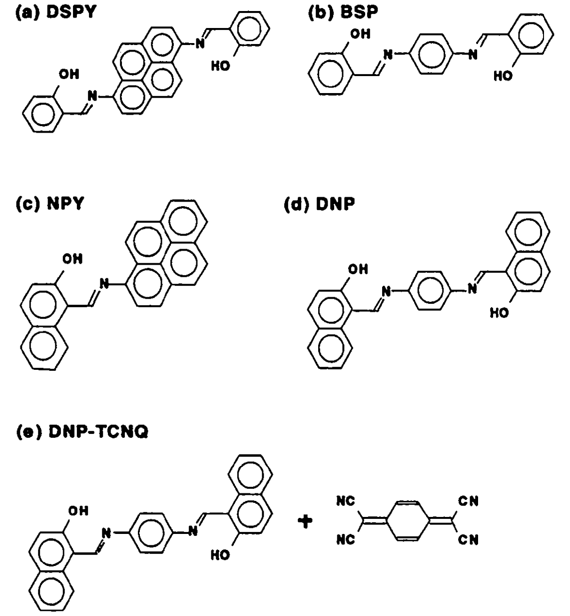

Figure 2
Molecular structures of the compounds studied.

3. Results and Discussion

Figure 3 shows the O *K*-edge NEXAFS spectra of the five SA derivatives. For comparison, the gas phase electron energy loss spectra of phenol (PH) (f) and *p*-benzoquinone (BQ) (g) (Francis & Hitchcock 1992), and the simulated spectra of SA (h) are also shown. The peaks I and II in the spectrum of BQ were assigned to the transitions from the O1s level to the π^* orbitals and the feature III in the spectrum of PH was attributed to the σ^*(OH) excitation with possible contribution from 1s $\rightarrow$ π^* excitation (Francis & Hitchcock 1992). The features 1 and 2 in the spectra of NPY, DNP and DNP-TCNQ correspond to the peaks I and II of BQ, respectively, and can be ascribed to the NH-form with C=O double bond(s). The broad shoulder 3 of SA derivatives corresponds to the feature III of PH, and is attributed to the σ^*(O-H) + π^* excitations in the OH-form.

The amount of the NH-form can be estimated from the intensity of the peak 1. DSPY does not show this peak, indicating the absence of the NH-form. The spectrum of BSP shows a small rise at about 531 eV in the expanded spectrum (hatched region), suggesting that BSP has a small but finite amount of the NH-form. The other data indicates the increase of the NH-form in the order of NPY, DNP, and DNP-TCNQ. Similar results were obtained from the N *K*-edge spectra (not shown.).

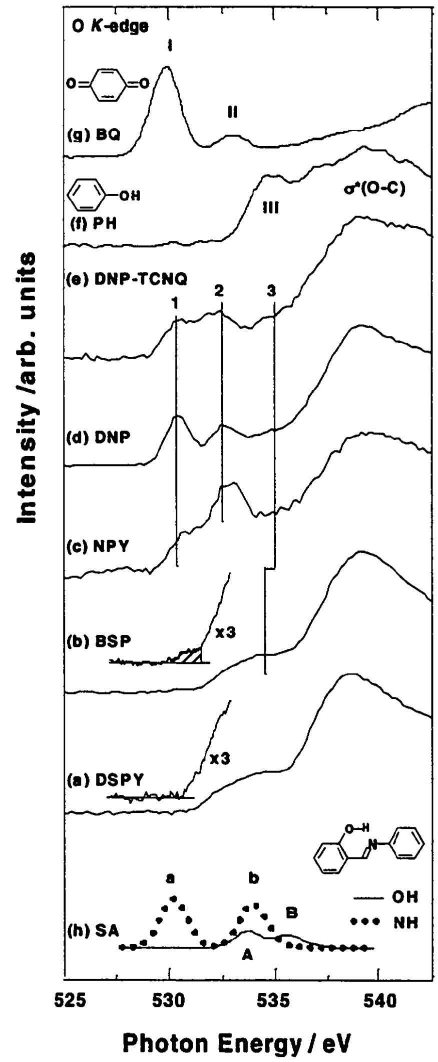

Figure 3
O *K*-edge NEXAFS spectra of (a) DSPY, (b) BSP, (c) NPY, (d) DNP, and (e) DNP-TCNQ, and the electron energy loss spectra of gas phase (f) phenol (PH) and (g) *p*-benzoquinone (BQ). The simulated spectra (h) by ab initio MO calculations of SA in the OH-form (solid line) and the NH-form (dotted line) are also shown.

The assignments by MO calculations are consistent with those from the comparison with the spectra of related compounds. The peaks 1 and 2 should correspond to the peaks a and b in the simulated spectrum of the NH-form, respectively, and the peak 3 corresponds to the peaks A and B in the simulated spectrum of the OH-form. The good correspondence with the observed results demonstrates the usefulness of the present theoretical analysis for assigning the spectral features for the complex systems.

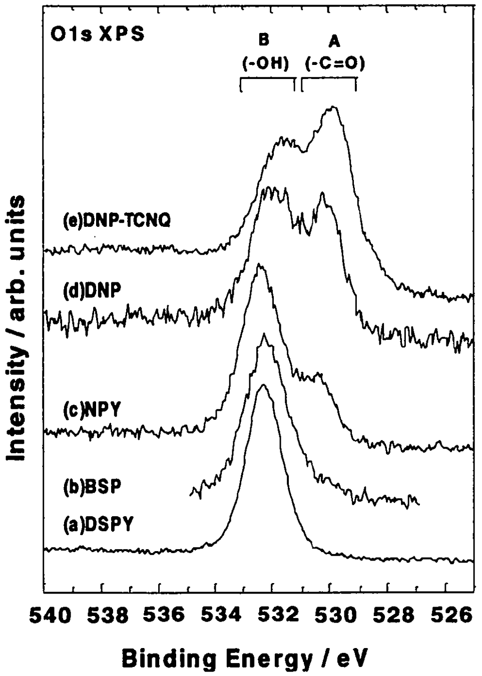

Figure 4
O1s XPS of (a) DSPY, (b) BSP, (c) NPY (d) DNP, and (e) DNP-TCNQ.

The XPS results offer an independent way of examining the tautomerism. In Figure 4, the O1s XPS spectra of SA derivatives are shown. The spectra of BSP, NPY, DNP, and DNP-TCNQ can be decomposed into two peaks A and B. On the other hand, the spectrum of DSPY shows only peak B. Comparison with the results for BQ (530.8 eV) and *p*-hydroquinone (HO-C6H4-OH) (532.2 eV) (Ohta et al. 1974) ascribes the peak A to the C=O group in the NH-form and the peak B to the OH group in the OH-form, respectively. The relative amounts of tautomers can be estimated from the N1s and O1s spectra by the curve fitting and are listed in Table 1. The results from N1s and O1s spectra are similar, and also consistent with those from NEXAFS. These results show that quantitative estimation could be successfully performed by XPS.

Takeda and co-workers estimated the energy differences between the tautomers from the relaxation time of proton NMR in BSP (Takeda et al. 1992). Recently, they also estimated the energy differences in DNP from the detailed analysis of ^{15}N-CP/MAS NMR measurements and the relaxation time of proton NMR (Takeda et al. 1998). If we assume the Boltzmann distribution and the reported values of the energy differences, the relative population of each tautomer can be determined. For BSP and DNP, the OH-form population is 85 % and 60 % at room temperature (T=300K), respectively. These values agree well with the results from XPS.

Table 1
Relative amounts of the OH-form tautomer estimated from N1s and O1s XPS spectra of SA derivatives.

Compounds	N1s	O1s
DSPY	100%	100%
BSP	96%	93%
NPY	80%	75%
DNP	60%	50%
DNP-TCNQ	-	40%

Finally, we discuss the tautomeric structures of these compounds, and demonstrate the usefulness of the NEXAFS method. Inabe et al. (1994) deduced the H-bonded structures by the bond length of C-O (r(C-O)) and density map from D-synthesis method. r(C-O) should be long for a pure OH-form and will become shorter with increasing weight of the NH-form. Comparison among the values of r(C-O) shows that DSPY is almost purely in the OH-form. On the other hand, DNP-TCNQ has the shortest r(C-O) among the compounds studied, indicating the largest contribution from the NH-form. NPY and DNP have a similar r(C-O), which are intermediate between those of DSPY and DNP-TCNQ. From these data, we can deduce increasing population of the NH-form in the order of DSPY < BSP < NPY ≈ DNP < DNP-TCNQ.

NEXAFS and XPS results are consist with the XD results. Thus the NEXAFS and XPS data firmly established the tautomeric structures of these SA derivatives. This result shows the usefulness of NEXAFS method for the investigation of the tautomerism.

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