An X-Ray Photoelectron Spectroscopic Study of Several Hydroxy Azo Compounds

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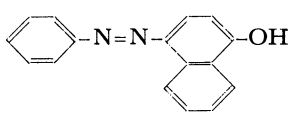
The tautomerism of several solid hydroxy azo compounds has been examined by X-ray photoelectron spectroscopy. It has been found that the proportion of enol and keto tautomers may be readily estimated from the relative intensities of the two peaks in the O(1s) electron spectrum which corresponds to the protonated and deprotonated oxygen atoms. The resonance structures of the sodium salt of 1-phenylazo-2-naphthol and 5-phenylazo-8-quinolinol have been discussed on the basis of the N(1s) and O(1s) electron binding energies.

Phenylazo derivatives of phenols and naphthols can exist either in the enol form (*e.g.* **1**) or in the keto form (*e.g.* **2**). Numerous investigations have been conducted to establish the structure in solution or solid by a variety of techniques *e.g.* visible and UV,[1] Raman,[2] IR,[3] NMR,[4] and X-ray diffraction analysis.[5] Phenylazo derivatives of phenol appear to exist in the enol form both in solution and the solid, whereas in the phenylazo derivatives of naphthols both forms coexist even in the solid state. There have been however few studies concerning a quantitative analysis of the tautomers in solid hydroxy azo compounds.[1e]



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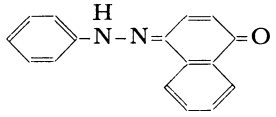

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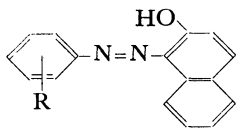
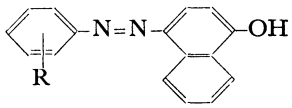
X-Ray photoelectron spectroscopy (XPS), which is sensitive to the charge distribution, is suitable for the detection of protonated atoms.[6] The purpose of the present XPS study is to determine the proportions of enol and keto form tautomers of several solid hydroxy azo compounds, and furthermore, to examine the chemical structures of two compounds; the sodium salt of 1-phenylazo-2-naphthol and 5-phenylazo-8-quinolinol. In the former compound a mobile hydrogen atom is absent in the molecule and in the latter a mobile hydrogen atom is considered fixed by an intramolecular hydrogen bond.

Experimental

The X-ray photoelectron spectra were measured on an AEI ES200 spectrometer. Mg $K\alpha$ (1253.6 eV) X-ray radiation was used as the excitation source. The samples were ground to a powder and dusted on to double-backed adhesive tape. The measurements were conducted at room temperature under a vacuum of about 10^{-7} Torr. The binding energy of the C(1s) electron peak was used as the energy standard throughout the present work and has been taken to be 285.0 eV. The reproducibilities of the values thus obtained were within ± 0.1 eV. Appreciable X-ray damage was not observed throughout the experiments. All the compounds used and their binding energies are given in Table 1. Phenylazo, naphthylazo, and quinolylazo derivatives of naphthols were prepared by the standard diazo-coupling reaction with the naphthols. 5-Phen-

Table 1. Measured binding energies and proportions of keto tautomer

Compound	R	Binding energy/eV		R/%[a]	
		N(1s)	O(1s)	A[b]	B[c]
	*o*-OCH_3	400.4	533.3; 530.9	69	
	p-OCH_3	400.2	533.2; 531.2	32	55
	o-CH_3	400.5	533.1; 531.1	62	
	p-CH_3	400.4	533.0; 531.0	59	65
	H	400.5	533.0; 531.1	64	70
	o-Cl	400.5	533.0; 531.0	64	
	p-Cl	400.4	532.9; 531.1	53	65
	m-Cl	400.5	533.2; 531.3	69	65
	*p*-OCH_3	400.4	533.2; 530.9	60	65
	H	400.5	533.1; 531.0	73	80
5-Phenylazo-8-quinolinol		400.3; 399.4	532.9	≈0	
1-(2-Pyridylazo)-2-naphthol		400.5; 399.0	533.0; 530.9	76	
1-(8-Quinolylazo)-2-naphthol		400.3; 398.9	533.0; 530.8	68	
1-(1-Naphthylazo)-2-naphthol		400.5	533.0; 531.0	69	
4-(Phenylazo)phenol		400.3	533.1	≈0	
1-Phenylazo-2-naphthol sodium salt		400.5; 399.0	531.0		
1,1′-Azonaphthalene		400.2			

a) The proportion of keto tautomer. b) The values estimated in this study. c) The reported values[1e] estimated from electronic spectra.

ylazo-8-quinolinol was obtained by diazo-coupling with 8-quinolinol in acetic acid.[7] 4-(Phenylazo)phenol and 1-(2-pyridylazo)-2-naphthol were obtained commercially and used after recrystallization from ethanol. The sodium salt of 1-phenylazo-2-naphthol was obtained by treating the naphthol with NaOH in a mixture of ethanol and water: the black crystals separated out were subject to hydrolysis by water and ethanol. Therefore, the crystals collected by filtration were rapidly washed with a small amount of alkaline ethanol and diisopropyl ether, and dried *in vacuo* at 90 °C. The salt thus obtained was brownish black. Found: C, 71.69; H, 4.42; N, 10.47%. Calcd for $C_{16}H_{11}N_2ONa$: C, 71.11; H, 4.07; N, 10.37%. 1,1'-Azonaphthalene and two nickel complexes of phenylazo derivatives of 2-naphthol as reference compounds were prepared according to the literature.[8,9] All compounds were checked by elemental analysis, and all compounds except for the sodium salt and the two metal complexes were also checked by melting point measurement.

Results and Discussion

The Determination of the Equilibria of Tautomers. The O(1s) electron spectrum of 1-phenylazo-2-naphthol is shown in Fig. 1. E_b in the figure indicates the binding energy. The spectrum clearly showed two peaks, which suggested the presence of two types of oxygen atoms in the molecule. The peaks with full-width at half-maximum height (FWHM) of approx. 1.5 eV indicated by the broken lines in the figure were obtained by graphical resolution. P_1 and P_2 indicate their peak heights in Figs. 1 and 2. The binding energy difference between the two peaks was 1.9 eV. The reported values of the difference between the O(1s) binding energies of protonated and deprotonated oxygen atoms have been in the range of 1.4—1.9 eV.[10] Furthermore, the O(1s) electron spectrum of 4-(phenylazo)phenol, which is known to exist as the pure azo compound from the IR study,[3] showed a single peak with a FWHM of 1.5 eV. The binding energy was very similar to that of the peak with the higher binding energy of 1-phenylazo-2-naphthol. Therefore, it appears to be reasonable to assign the peaks with high and low binding energies in Fig. 1 to the protonated and deprotonated oxygen atoms respectively.

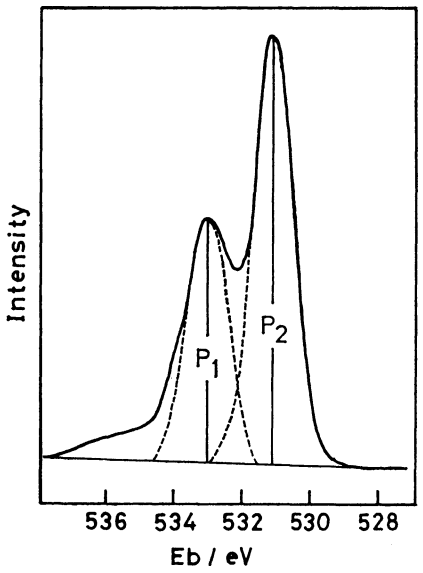


Fig. 1. O(1s) electron spectrum of 1-phenylazo-2-naphthol.

In XPS, the relative intensities of the peaks of a certain atom correspond to the relative amounts of the atom present in different states in the molecule. Therefore, it may be considered that the equation $100 \cdot P_2/(P_1+P_2)$ corresponds to the proportion(%) of the deprotonated oxygen atom and consequently, of the keto form tautomer in such a compound as 1-phenylazo-2-naphthol, which contains only two kinds of oxygen atoms in the molecule—protonated and deprotonated oxygens.

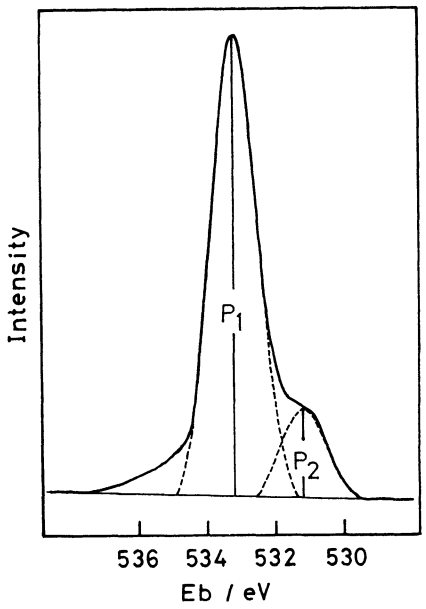


Fig. 2. O(1s) electron spectrum of 1-(*p*-methoxyphenylazo)-2-naphthol.

The O(1s) electron spectrum of 1-(*p*-methoxyphenylazo)-2-naphthol is shown in Fig. 2, as an example of a compound containing a methoxyl group in the molecule. It was found that the O(1s) binding energy of the oxygen atom of a methoxyl group was almost the same as that of a protonated oxygen atom in respect to the O(1s) electron spectra of the two nickel complexes. The O(1s) electron spectrum of bis[1-(*p*-methoxyphenylazo)-2-naphtholato]nickel(II) showed two peaks with nearly equal intensities, and that of bis(1-phenylazo-2-naphtholato)nickel(II) showed a single peak. The O(1s) electron binding energies of the former complex were 533.2 eV and 531.3 eV, and that of the latter was 531.3 eV.

Therefore, the single peak with the higher binding energy of the two in Fig. 2 can be assigned to the oxygen of the methoxyl group in addition to the protonated oxygen, and the other to the deprotonated oxygen. Consequently, in the case of a compound such as 1-(*p*-methoxyphenylazo)-2-naphthol, which contains a methoxyl group, it may be considered that the equation $100 \cdot P_2/(P_1'+P_2)$, where $P_1'=P_1-(P_1+P_2)/2$, corresponds to the proportion of the keto form tautomer.

The O(1s) electron spectra of all other naphthol derivatives showed two types of peak similarly to 1-phenylazo-2-naphthol.

The proportions of keto form tautomer estimated in the above ways are given in Table 1, together with the reported values derived from the electronic spectra by use of the potassium bromide disc.[1e] The values are comparable with the reported values. In this study, errors of approx. 5% were unavoidable due to the incompleteness of graphical resolution.

It appears that the XPS method is more suitable than the electronic spectra method for the determination of equilibria of tautomers in the solid state since the latter method involves considerable uncertainty in the values of the true energies and intensities of the bands of the individual tautomers. Furthermore, it has been said that the spectra obtained by the potassium bromide disc method are not free from the influence of the diluent.[1f]

The N(1s) electron spectra of all hydroxy azo compounds except for the three hydroxy azo compounds containing heterocyclic nitrogen atoms and the sodium salt of 1-phenylazo-2-naphthol showed a single peak with a FWHM (≈1.6 eV) and a binding energy similar to that of a reference compound 1,1'-azonaphthalene, which exists in the pure azo form. Therefore, it was impossible to examine the equilibria of the tautomers on the basis of the N(1s) spectra.

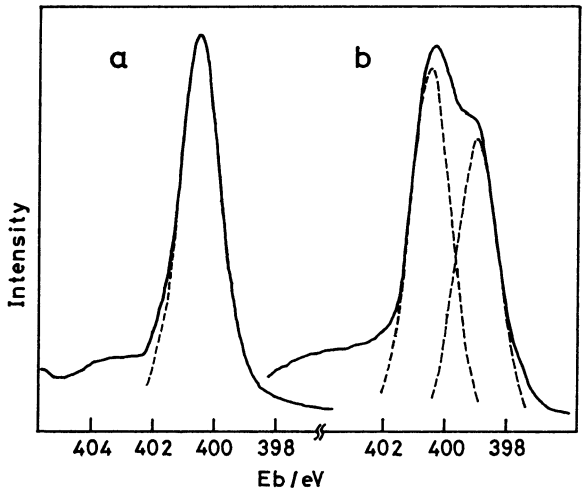
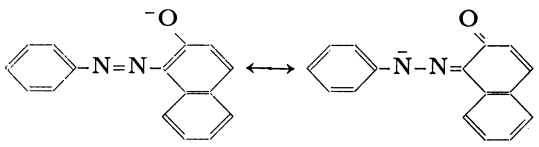


Fig. 3. N(1s) electron spectra of a: 1-phenylazo-2-naphthol and b: its sodium salt.

The Sodium Salt of 1-Phenylazo-2-naphthol. The N(1s) spectra of 1-phenylazo-2-naphthol and its sodium salt are shown in Fig. 3. The N(1s) spectrum of 1-phenylazo-2-naphthol showed a single peak, suggesting that the charge densities on the three types of nitrogen atoms, the nitrogen atoms of the azo group, the protonated and deprotonated nitrogen atoms of the hydrazono group, are almost equal. The spectrum of the salt showed two comparable peaks, which suggested the presence of two types of nitrogen atom. The peaks indicated by the broken lines in the figure were obtained by graphical resolution, as were those in Fig. 4. Furthermore, the O(1s) binding energy of the salt was very close to those of the keto form oxygen of hydroxy azo compounds. The results suggest the following resonance contribution:



The inequality in intensities of the two peaks of the salt in Fig. 3(b) may be due to an impurity (probably, 1-phenylazo-2-naphthol produced by hydrolysis of the salt) in the sample. The O(1s) spectrum of the salt showed a peak with some intensity around the energy (533 eV) corresponding to a protonated oxygen atom.

5-Phenylazo-8-quinolinol. The O(1s) electron spectrum of 5-phenylazo-8-quinolinol showed a single peak with a FWHM of 1.6 eV. From its binding energy, the peak was assigned to the protonated oxygen atom. This is consistent with the results[11] from the electronic spectra that 5-phenylazo-8-quinolinol exists predominantly in the enol form in solution due to the presence of an intramolecular hydrogen bond between the heterocyclic nitrogen and the hydroxyl hydrogen.

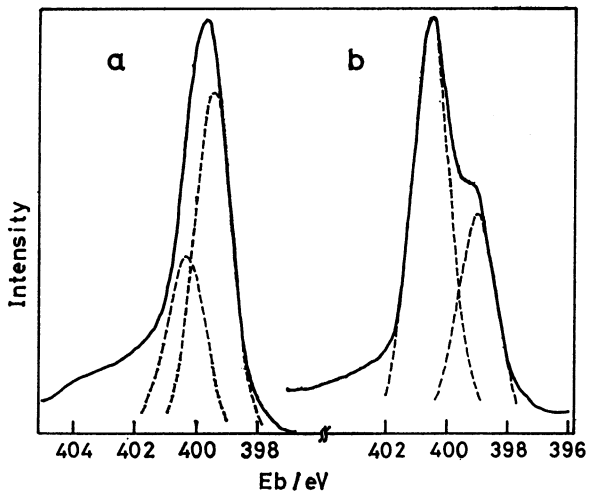


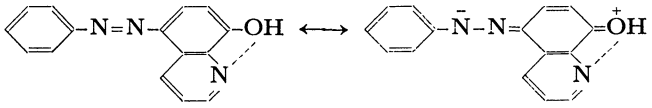
Fig. 4. N(1s) electron spectra of a: 5-phenylazo-8-quinolinol and b: 1-(2-pyridylazo)-2-naphthol.

The N(1s) spectra of 5-phenylazo-8-quinolinol and 1-(2-pyridylazo)-2-naphthol are shown in Fig. 4. Both spectra showed two peaks with an intensity ratio of approx. 2: 1. The N(1s) spectrum of 1-(8-quinolylazo)-2-naphthol was very similar to that of 1-(2-pyridylazo)-2-naphthol.

The peak with the lower binding energy of the two in 1-(2-pyridylazo)-2-naphthol and 1-(8-quinolylazo)-2-naphthol can be readily assigned to the heterocyclic nitrogen atom and the other to the nitrogen atoms of the azo group, by comparison with the N(1s) spectra of 1-phenylazo-2-naphthol and 1-(1-naphthylazo)-2-naphthol. That is, the N(1s) binding energy of the heterocyclic nitrogen atom is approximately 399.0 eV.

Therefore, it appears reasonable to assign the two peaks in 5-phenylazo-8-quinolinol with high and low binding energies to the nitrogen atom adjacent to the quinoline ring in the azo group and the remaining

nitrogen atom of the azo group in addition to the heterocyclic nitrogen atom respectively. The inequality of the two nitrogen atoms of the azo group may be caused by the following resonance:[3a)]



Here, the presence of an intramolecular hydrogen bond may stabilize the dipolar form, since the N(1s) spectra of all the hydroxy azo compounds having no such intramolecular hydrogen bond did not show any inequality for the two nitrogen atoms of the azo group.

The intramolecular hydrogen bond appears to be relatively strong, since the O(1s) binding energy of 5-phenylazo-8-quinolinol was not larger than those of the other hydroxy azo compounds. In fact, the N(1s) binding energy of the heterocyclic nitrogen atom was 0.4—0.5 eV higher than those of 1-(2-pyridylazo)-2-naphthol and 1-(8-quinolylazo)-2-naphthol.

In 5-phenylazo-8-quinolinol the contribution of the resonance structure with unit negative charge on the nitrogen atom of the azo group appears to be smaller than that in the sodium salt of 1-phenylazo-2-naphthol from the following result. The differences between the N(1s) binding energies of the two nitrogen atoms of the azo group are 0.9 eV for the former compound and 1.5 eV for the latter.

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