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X-Ray Photoelectron Spectroscopy of Aminobenzoic Acids and Anthranilic Acid Chelates

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Synopsis. Photoelectron spectra of three isomers of aminobenzoic acid and several metal chelates of *o*-isomer were measured. It was confirmed that *o*- and *p*-isomers exist in the non-polar form and *m*-isomer in the dipolar. In the chelates the trend was for the N(1s) chemical shifts to increase in parallel with the metal electronegativities.

It has been derived1) from IR spectroscopy that *m*-amino-benzoic acid in the solid state exists in the dipolar form, while *o*- and *p*-isomers exist in the non-polar form. The *o*-isomer(anthranilic acid) exhibits a polymorphic transition;2) its crystal structure for the form stable at room temperature has been determined from the X-ray diffraction data. It was found that there are two non-equivalent molecules per unit cell in the space group $P2_1cn$.3)

Khan and Srivastava4) deduced from X-ray and IR studies of the molecular stucture of *o*-isomer that the unit cell contains two equivalent molecules.

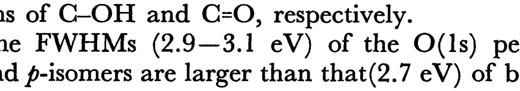
The purpose of this paper is to report the results by X-ray photoelectron spectroscopy (XPS) for the molecular structure of *o*-, *m*-, and *p*-isomers and for the chemical shift, the change in the N(1s) electron binding energy of anthranilic acid on complex formation.

The X-ray photoelectron spectra were measured on an AEI ES200 spectrometer. Al $K\alpha$ (1486.6 eV) X-ray radiation was used as the excitation source. The samples were ground to powder and then dusted onto a double-backed adhesive tape. The measurements were run at room temperature under a vacuum of about 10^{-7} Torr. The binding energy of the C(1s) peak was used as the energy standard throughout the present experiments; it was taken to be 285.0 eV. All the compounds measured are given in Table 1. Three isomers of aminobenzoic acid of an analytical grade were used after recrystallization from ethanol, and in the case of *o*-isomer after recrystallization from acetic acid,2) which was employed to obtain the form stable at room temperature. All the anthranilic acid chelates with a ligand–metal ratio of 2 : 1 were prepared based upon the literature methods.5)

The O(1s), N(1s), and C(1s) electron spectra of *o*-, *m*-, and *p*-aminobenzoic acids are shown in Fig. 1; their measured binding energies are given in Table 1. Two peaks were observed in the C(1s) electron spectra for all the isomers. It was determined that the one with higher binding energy corresponds to the carbon of the substituent group, and the other to the carbon of the benzene ring. The N(1s) electron binding energies of *o*- and *p*-isomers were about 2 eV lower than that of *m*-isomer. The O(1s) electron peak of *m*-isomer was narrower in full-width at half-maximum height (FWHM) and about 1—2 eV lower in binding energy, compared with those of *o*- and *p*-isomers. The O(1s) spectra of *o*- and *p*-isomers both have a broad peak, which suggests the presence of at least two kinds of oxygen atoms. The two peaks, a and b, with the different binding energies shown by the broken lines in the figure, were obtained by a graphical resolution of the peak of *p*-isomer.

In view of the stuctures4,6) of *o*- and *p*-isomers determined from X-ray and IR analyses, it seems that the two peaks, a and b, in Fig. 1 correspond to the oxygen atoms of C–OH and C=O, respectively.

The FWHMs (2.9—3.1 eV) of the O(1s) peaks of *o*- and *p*-isomers are larger than that(2.7 eV) of benzoic acid, which is the same value as acetic acid7) in the solid state. Such an increase of the FWHM in *o*- and *p*-isomers may be attributable to the contribution of a resonance structure, as shown below: This contribution has the possibility of increasing the difference between the electron densities on the two oxygens of the carboxylate group, which would give rise to the broadening of the O(1s) peak. Benzoic acid can not reasonably have the above resonance. That the FWHM of *o*-isomer is about 0.2 eV smaller than that of *p*-isomer may be attributable to the decrease of such resonance due to steric hindrance in the former, which has been suggested from IR.8)



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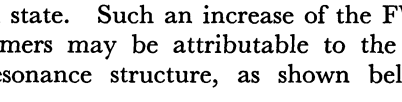

In the zwitterion structure of *m*-isomer,1) the N(1s) and O(1s) peaks may correspond to the positively charged nitrogen atom and the negatively charged oxygen atoms of the carboxylate group. The C(1s) binding energy of the carboxylate group of the *m*-isomer is about 1 eV lower than those of the other two isomers. This can be explained by arguing that the electron density on the carbon atom of the carboxylate group in the former becomes larger than those of the carboxyl group in the latter, because of the delocalization of a unit negative charge within a carboxylate group.

Although *o*-isomer crystallized from acetic acid has been reported to have in part a zwitterion structure,3) this was not confirmed by this XPS study at all.

The N(1s) and O(1s) electron spectra of all the anthranilic acid metal chelates and sodium salt were single peaks with the FWHMs of 1.6—1.8 eV and 1.7—1.9 eV, respectively, except that the FWHMs of the O(1s) peaks of Pd and Pt chelates were 2.1—2.2 eV.

In the charge-potential model,6) the chemical shift can be expressed in terms of the charge on the atom

Table 1. Measured binding energies and frequencies

Samples		Binding energy (eV)[a]				χ[d]	ν_{N-H}[e]	ν_{COO^-}[f]
		C(1s)[b]	N(1s)	ΔE[c]	O(1s)			
Aminobenzoic acids	*o*-	289.0	399.6		533.1 (2.9) (533.8, 532.4)[g]		3450	
	m-	288.3	401.6		531.5 (1.8)			
	p-	289.0	399.7		533.1 (3.1) (533.9, 532.4)[g]			
Benzoic acid		289.1			533.0 (2.7)			
Sodium salt of anthranilic acid		288.4	399.3		531.3 (1.7)		3400	1510
Anthranilic acid chelates	Pt	288.4	400.5	0.9	531.6 (2.1)	2.2	3140	1555
	Pd	288.3	400.3	0.7	531.6 (2.2)	2.2	3150	1550
	Cu	288.4	399.9	0.3	531.4 (1.9)	1.9	3260	1543
	Ni	288.6	399.9	0.3	531.4 (1.9)	1.8	3280	1535
	Mn	288.5	399.7	0.1	531.5 (1.9)	1.5	3290	1535
	Hg	288.3	400.1	0.5	531.3 (1.8)	1.9	3250	1540
	Cd	288.6	399.8	0.2	531.5 (1.8)	1.7	3280	1530
	Zn	288.6	399.8	0.2	531.4 (1.9)	1.6	3280	1535

The numbers in parentheses indicate the full-width at half-maximum height. a) Uncertainties are less than or equal to ±0.1 eV. b) The C(1s) electron binding energy of a substituent group. c) The N(1s) chemical shift. d) Pauling electronegativity of the metal. e, f) The N–H stretching and the COO^- antisymmetrical vibration frequencies (cm^{-1}), respectively, determined in Nujol mull on a IR spectrometer, model IR-G, of Japan Spectroscopic Co., Ltd. g) The values obtained by a graphical resolution.

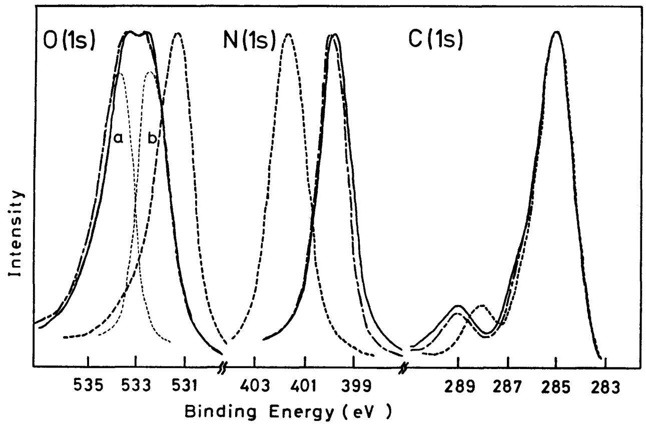

Fig. 1. O(1s), N(1s), and C(1s) photoelectron spectra of aminobenzoic acids.
——: *o*-Isomer, ------: *m*-isomer, —·—·—: *p*-isomer.

and the Coulomb potential energy of an electron due to the other atoms in the molecule. In this study, however, it was assumed that the chemical shift is dominated by the charge on the atom concerned, since the compounds studied here are covalent and their structures are similar. Therefore, the N(1s) chemical shifts in all the chelates are considered to be due to the decrease in the electron density on the nitrogen atoms caused by the coordination of lone-pair electrons of the nitrogen atoms to the metal.

The N(1s) chemical shifts tended to increase in parallel with the metal electronegativities. This can be explained by arguing that the covalent character of the bonds between the metal ions and the ligand increases with the metal electronegativity. A more covalent coordinate bond is considered to decrease the electron density on the donor atoms, which would appear in the increase of the binding energies.

It has previously been demonstrated by IR that the coordination of amino groups to metals results in appreciable decreases in the frequencies of the N–H stretching vibrations. These changes become larger with increasing covalent character of the N–M bonds.[9] There seems to be a certain reasonable relation between the N(1s) chemical shift and the N–H frequency, the N(1s) chemical shift increasing with decreasing N–H frequency.

All the binding energies and the FWHMs of the O(1s) peaks of the metal chelates were similar to those of sodium salt rather than those of free anthranilic acid. The C(1s) binding energies of the carboxylate group for the chelates (288.3—288.6 eV) were also similar to that of sodium salt (288.4 eV).

It has been concluded from the IR study that as the bonding of the carboxylate groups with a metal atom becomes more covalent the absorption peak for the antisymmetrical vibration of the COO^- groups shifts to higher frequencies.[10] All the frequencies of the chelates are larger than that of sodium salt, as shown in Table 1. Furthermore, the O(1s) binding energies of almost all chelates are slightly larger than that of sodium salt.

These results suggest that the COO^-–M^{2+} bonds in anthranilic acid chelates are not so essentially ionic as in the case of sodium salt.

Sandhu *et al.*[11] have proposed a polymeric structure for the anthranilic acid metal chelates from IR and magnetic susceptibility measurements, and suggested that the stereochemistry around the metal ion is that of a distorted octahedron, with both oxygens of carboxylate bonded to two different metal atoms, though unequally. This inequality of the two oxygens of carboxylate may be associated with the present result that the FWHMs of the O(1s) peaks of the chelates are 0.1—0.5 eV larger than that of the sodium salt, as is shown in Table 1.

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