Resonace Raman Spectra of Acid-Base Indicators. II. Hydroxyarylazobenzene Derivatives

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The effects of pH on resonance Raman spectra of several hydroxyarylazobenzene-type acid-base indicators have been investigated. All the compounds examined show the azo-type spectra in basic solutions, while the neutral solution spectra are the azo-type for *p*-hydroxyphenyl compounds and the quinoid-type for α- and β-hydroxynaphthyl compounds. The spectrum of Tropaeoline O changes complicatedly along with the protonation and deprotonation on the pH change.

The acid-base indicators containing azo group can be classified into two categories, the amino and the hydroxy derivatives. Recently, we have investigated the resonance Raman spectra of some important amino-azo-type acid-base indicators, and have shown that the spectral pattern reflects clearly the structure change accompanying the color change.[1] When the neutral solution of an aminoazo-type indicator is acidified to pH below the color change interval, the azo-type base form is protonated at the azo group and is transformed into the quinoid-type acid form. This transformation gives rise to the replacement of azo bands by quinoid bands in resonance Raman spectra along with the red shift of λ_{max} in visible absorption spectra. On the contrary, the color change of hydroxyazo-type acid-base indicators occurs mostly in the basic pH region, in such a way that λ_{max} shifts to red on addition of alkali to the neutral solution. The tautomerism between the azo and the quinoid forms is conceivable for the acid form. Extensive studies on visible and ultraviolet spectra of hydroxyarylazo compounds have shown that the tautomeric ratio varies widely depending on the nature of aromatic rings and substituents.[2-7] Accordingly, the color change of hydroxyazo-type indicators cannot be elucidated from such a simple correlation between λ_{max} and the structure as seen for amino-azo-type indicators for which the reddish color in acidic solutions is due to the quinoid form.[1] In this respect, it is of importance to clarify how the molecular vibrations of hydroxyazo derivatives are affected by the structure change underlying the color change.

In this paper, we report the resonance Raman spectra of several representative hydroxyphenyl- and hydroxynaphthylazobenzene derivatives, and discuss the structures of these compounds at various pH by referring to spectra of related compounds and deuteration effects.

Experimental

The hydroxyarylazobenzene derivatives taken up in this work were obtained from commercial sources, and were recrystallized several times from water or ethanol. In Table 1, the λ_{max} in the visible and ultraviolet absorption spectra and the color change intervals of these compounds are listed together with the abbreviations to be used in the text. The Raman spectra between 1800 and 1000 cm^{-1} were recorded on a JEOL S-1 laser Raman spectrophotometer by using the 488 nm excitation line of a coherent Ar^+ laser.

Each sample was sealed in a 1 mm capillary tube. The pH of aqueous solutions was adjusted by using 1 M HCl, 1 M NaOH and the phosphate and borate buffers. For the deuteration of active hydrogen atoms, the stock solutions of 1 M DCl and 1 M NaOD in heavy water were prepared and used as described in the previous paper.[1] Reagent grade ethanol and *n*-hexane were used as the solvents for SuI. The concentration dependence of Raman intensities was roughly surveyed for each compound, and the optimum concentration was found to fall between 10^{-2} and 10^{-4} M. The decomposition of samples due to the irradiation of the excitation beam was not detected except for the cases of AY in the neutral solution and SuI in 50% ethanol. The absorption spectra between 330 and 600 nm were recorded on a Shimadzu W-40 spectrophotometer.

Results and Discussion

p-Hydroxyphenylazo Derivatives. The resonance Raman spectra of HAS in neutral aqueous solution and

TABLE 1. ABSORPTION MAXIMA AND COLOR CHANGE INTERVALS

Compound	Abbr.	Absorption maximum (nm)		Color change interval (pH)
		Acid form	Base form	
p-Hydroxyazobenzenesulfonic acid	HAS	351	435	
m-Nitrobenzeneazosalicylic acid (Alizarine yellow GG)	AY	352	452	10.2—12.0[d]
p-(2-Hydroxy-1-naphthylazo)benzene (Sudan I)	SuI	475[a]	435[b]	
p-(4-Hydroxy-1-naphthylazo)benzenesulfonic acid (Orange I)	OrI	474	514	7.4—8.8[d]
p-(2-Hydroxy-1-naphthylazo)benzenesulfonic acid (Orange II)	OrII	484	455 505[b]	10.9—11.9[e]
p-(2,4-Dihydroxy-phenylazo)benzenesulfonic acid (Tropaeoline O)	TrO	427[c]	491	11.1—12.7[d]

a) in EtOH. b) in 30% EtOH. c) The absorption maxima at pH 0.2 and 4.0 are at 440 and 380 nm, respectively. d) I. M. Kolthoff, "Acid-Base Indicators," The Macmillan Co., New York (1937), p. 147. e) Ref. 6.

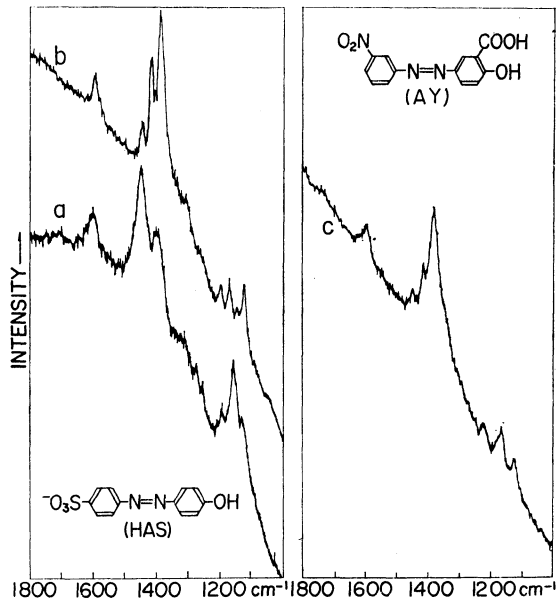


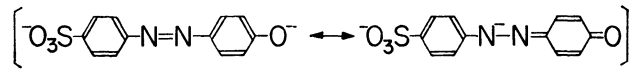
Fig. 1. Resonance Raman spectra of HAS and AY: (a) 1×10^{-2} M HAS in H_2O, slit width 27 cm^{-1}; (b) 1×10^{-3} M HAS in 0.5 M NaOH, slit width 14 cm^{-1}; (c) 1×10^{-3} M AY in 0.5 M NaOH, slit width 14 cm^{-1}.

of HAS and AY in 0.5 M NaOH are shown in Fig. 1. In all these spectra, several bands appear commonly in the region between 1600 and 1000 cm^{-1}, the strongest being near 1400 cm^{-1}. This spectral pattern is similar to those of *p*-phenylazophenol in methanol[8] and methyl-orange in water.[1,9] The strong band at 1445 cm^{-1} in Fig. 1a arises clearly from the stretching vibration of the *trans* N=N group, indicating that the monovalent anion of HAS exists dominantly as the azo form. This result is in agreement with the previous conclusions based on visible and ultraviolet spectra.[3,4] The assignment of the remaining bands was easily made as

Table 2. Observed frequencies and assignments for HAS and AY

HAS		AY	Assignments
H_2O	0.5M NaOH	0.5M NaOH	
1600 vw	1598 w	1597 w	Benzene ring
	1447 w	1450 w	Benzene ring
	1417 m	1415 m	Benzene ring
1445 s	1386 s	1382 s	N=N str.
1400 m			Benzene ring
1195 sh	1195 w	1223 w	Benzene ring
1150 m	1167 w 1145 vw	1167 m	C–N str.
1125 sh	1122 w	1123 w	Benzene ring

shown in Table 2 from analogy with the base form of methyl orange and related compounds.[1] The good correspondence of weak bands between HAS and AY in basic solutions shows that vibrations of the $-SO_3^-$, $-NO_2$, and $-CO_2^-$ groups do not participate in the resonance Raman effects of the hydroxyazo compounds treated in this work. The shift of the N=N stretching frequency from 1445 to 1386 cm^{-1} on going from the acid form to the base form of HAS indicates that the N=N bond order decreases on the deprotonation of the phenolic OH group. Accordingly, the divalent HAS anion can be described as a resonance hybrid



in which the contribution of the azo structure is predominant but that of the quinoid structure is not negligible. The red shift in the visible absorption on the deprotonation of azophenol derivatives may be related to this contribution of the quinoid structure.

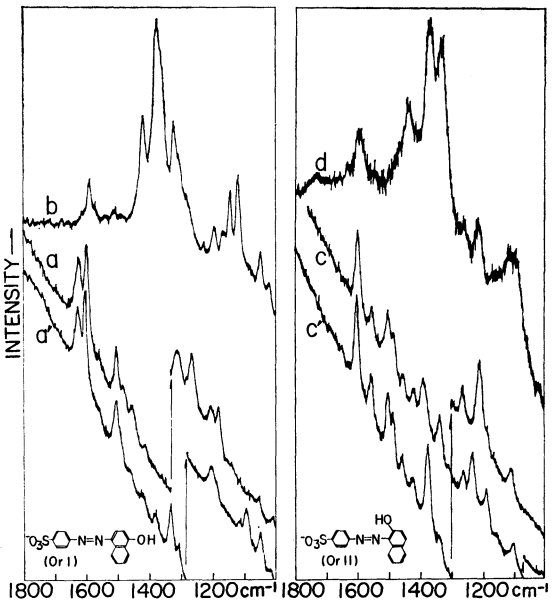


Fig. 2. Resonance Raman spectra of 1×10^{-3} M OrI and OrII: (a) OrI in H_2O, slit width 14 cm^{-1}; (a') OrI in D_2O, slit width, 14 cm^{-1}; (b) OrI in 0.5 M NaOH, slit width 27 cm^{-1}; (c) OrII in H_2O, slit width 14 cm^{-1}; (c') OrII in D_2O, slit width 14 cm^{-1}; (d) OrII in 0.5 M NaOH, slit width 27 cm^{-1}.

Hydroxynaphthylazo Derivatives. Figure 2 shows the resonance Raman spectra of hydroxynaphthylazobenzenesulfonic acids in neutral and basic solutions. In contrast to the case of HAS, the spectra of these naphthylazo derivatives undergo significant changes on the increase of pH from the neutral region to the basic region above the color change interval. In the resonance Raman spectrum of OrI in the neutral solution, there is no strong band around 1400 cm^{-1} assignable to the N=N stretching vibration. Instead, this spectrum shows medium to strong bands at 1629, 1508, and 1292 cm^{-1} in analogy with the previously reported spectra of *p*-aminoazobenzene derivatives in acidic solutions.[1] By referring to the latter case and also to the infrared spectra in the solid state,[10,11] most of the resonance Raman bands presently observed for OrI are assigned reasonably to vibrations of the quinoid form as shown in Table 3. Although OrI has a naphthalene ring in place of the benzene ring of *p*-aminoazobenzene derivatives, the spectral change on deuteration between 1400 and 1000 cm^{-1} of the former is quite analogous to that observed for the latter.[1] This result indicates that only the bands related to the structure C=N–NH–C are deuteration sensitive in both cases.

Table 3. Observed frequencies and assignments of the neutral solutions of OrI, OrII, and SuI

OrI		OrII		SuI		Assignments
H_2O	D_2O	H_2O	D_2O	EtOH	EtOD	
1629 m	1629 m					C=C str.
1603 m	1603 m	1601 s[a)]	1601 s[a)]	1608 s[a)]	1607 s[a)]	Benzene ring
1508 m	1506 m	1505 m	1504 m	1505 m	1500 m	Benzene ring
	1380 w	1390 m	1375 s	1396 m	1381 s	C–C str.
1292 w	1333 m	1262 w	1262 w	1270 vw	1263 w	C–N str.
1208 w	1205 m	1235 m	1210 s	1236 s	1213 s	N–N str.
	1095 w					N–D def.

a) Contributed also by the C=C stretching vibration.

The absence of the resonance Raman bands due to the azo form of OrI in the neutral solution seems at first sight to indicate that OrI exists exclusively as the quinoid form. There have been evidences from visible and ultraviolet spectra, however, for the existence of the azo form as the minor component in solutions of various 4-phenylazo-1-naphthol derivatives in polar solvents.[5)] The present result does not conflict with the visible and ultraviolet data since the quinoid form showing the λ_{max} near 480 nm should be much more sensitive to the resonance Raman effect by the 488 nm excitation than the azo form showing the λ_{max} near 420 nm.

The resonance Raman spectrum of OrII in the neutral solution resembles that of OrI in positions and relative intensities of several bands (see Table 3), suggesting that OrII takes the quinoid form predominantly in the neutral solution. OrII shows, however, a number of medium to weak bands which are not observed for OrI. The presence of these bands may be taken to reflect the structural difference between the *o*-quinoid and the *p*-quinoid rings, but it is also possible to attribute these bands of OrII, especially the medium band at 1390 cm^{-1}, to the azo form which may exist as the minor component. In order to clarify this point, we have recorded the resonance Raman spectra of SuI, for which the solvent effect on the visible and ultraviolet spectra has been studied in detail to discuss the tautomeric equilibrium between the azo and the quinoid forms.[5)] The result seems to support the assignment of the 1390 cm^{-1} band to the *o*-quinoid structure. If this band is due to the azo form, an appreciable increase of its relative intensity should occur on the change of solvent from ethanol to *n*-hexane, since the azo form is the major component in *n*-hexane but is not in ethanol according to the visible and ultraviolet spectra.[5)] As shown in Fig. 3, however, we observed no appreciable difference in the relative intensity of the 1396 cm^{-1} band between the ethanol and the *n*-hexane solutions of SuI.

In basic solutions, the hydroxynaphthyl derivatives show the same pattern of resonance Raman spectra as HAS, giving rise to the strong N=N stretching band around 1380 cm^{-1}; see Table 4. Accordingly, the base form of hydroxynaphthyl derivatives is the divalent anion existing as the resonance hybrid in which the contribution of the azo structure is predominant. The difference between OrI and OrII in the spectra of basic solutions is far less conspicuous than that in case of neutral solutions. This result reflects well the selective enhancement of the band intensities for vibrations of the chromophore group in the resonance Raman effect. It is expected that the vibrations of the C–N=N–C group are not practically affected by the position of the substituent on the aromatic ring, whereas the structure difference between the *o*-quinoid and the *p*-quinoid rings should give rise to appreciable differences in vibrational modes and frequencies.

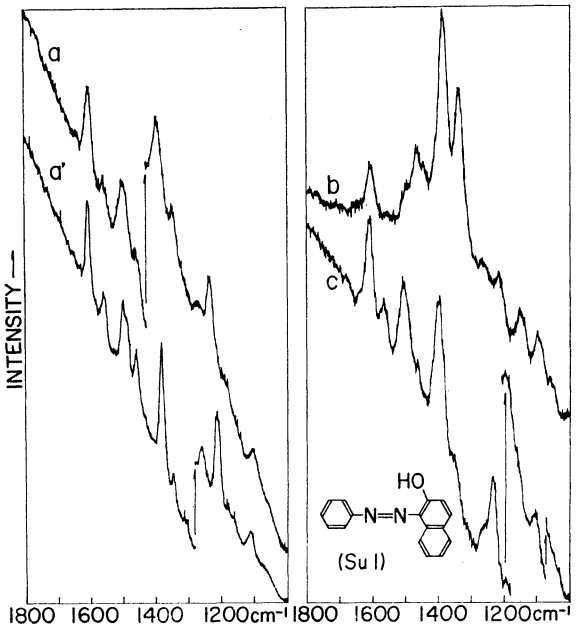


Fig. 3. Resonance Raman spectra of 1×10^{-3} M SuI: (a) in EtOH, slit width 27 cm^{-1}; (a') in EtOD, slit width 14 cm^{-1}; (b) in a 3:7 mixture of EtOH and 0.5 M NaOH, slit width 14 cm^{-1}; (c) in *n*-hexane, slit width 27 cm^{-1}.

Table 4. Observed frequencies and assignments for the basic solutions of OrI, OrII, and SuI

OrI	OrII	SuI	Assignments
1595 w	1595 w	1600 w	Ring vib.[a)]
1420 m	1440 w	1450 m[b)]	Ring vib.[a)]
1378 vs	1372 vs	1385 vs	N=N str.
1325 m	1345 s	1335 m	Ring vib.[a)]
1190 w	1215 w	1210 w	Ring vib.[a)]
1120 m	1125 w	1145 m	C–N str.

a) Vibrations due to the benzene or naphthalene ring.
b) Overlapped by the ethanol band.

Tropaeoline O. The visible and ultraviolet absorption spectrum of TrO changes in four steps on the pH

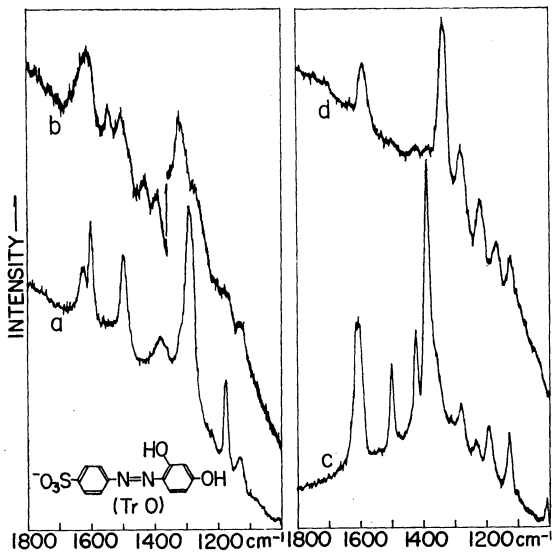


Fig. 4. Resonance Raman spectra of 1×10^{-3} M TrO: (a) in 1 M HCl, slit width 14 cm^{-1}; (b) in pH 4.0 buffer, slit width 27 cm^{-1}; (c) in pH 9.2 buffer, slit width 14 cm^{-1}; (d) in 1 M NaOH, slit width 14 cm^{-1}.

change of the solution from 1 M NaOH to 1 M HCl (see footnote,[c] Table 1). The resonance Raman spectra corresponding to these steps are different from one another as shown in Fig. 4. These spectral changes are thought to represent the stepwise protonation of TrO taking place according to Chart 1. The band assignments for the four spectra of TrO are summarized in Table 5. When dissolved in 1 M NaOH, TrO exists as the completely deprotonated trivalent anion and shows an azo-type resonance Raman spectrum in which the strongest band is observed at 1341 cm^{-1}. In analogy with the case of so far discussed monohydroxy compounds, the trivalent anion of TrO can be described as a resonance hybrid contributed mainly by the azo structure. The pattern of the resonance Raman spectrum of TrO in the pH 9.2 buffer solution is different from any of those already mentioned. This spectrum involves a number of bands attributable to the quinoid form of the divalent anion, *e.g.*, the strong

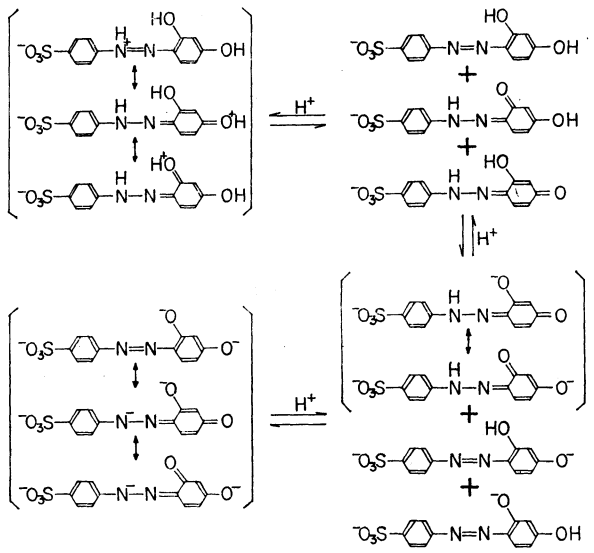


Chart 1

Table 5. Observed frequencies and assignments for TrO

1M HCl	pH 4.0 Buffer	pH 9.2 Buffer	1M NaOH	Assignments
1628 m	1610 s[a]	1618 s[b]		C=C str.
1601 s		1603 s[b]	1595 m	Benzene ring
1500 s	1500 m	1500 m		Benzene ring
1385 w	1390 w			C–C str.
		1387 vs	1341 vs	N=N str.
1290 vs	1320 s	1278 w		C–N str.(Quinoid)
			1282, 1221) m	Benzene ring
1175 m				N–N str.
		1193 w	1170 w	C–N str.(Azo)
1130 w	1130 sh	1130 m	1125 w	Benzene ring

a) Contributed also by the benzene ring vibration.
b) Measured with the slit width 6.8 cm^{-1}.

band at 1500 cm^{-1} and the weak band at 1278 cm^{-1}, of which the latter disappears on deuteration. The appearance of a very strong band at 1387 cm^{-1} in this spectrum suggests also that the azo form exists in an appreciable amount at pH 9. The resonance Raman spectrum of TrO in the pH 4 buffer solution is similar to those of the hydroxynaphthyl derivatives in neutral solutions, and is therefore due clearly to the quinoid form. It is not probable, however, that the monovalent anion of TrO takes the quinoid form exclusively in the pH 4 buffer solution, since the λ_{max} at pH 4 lies near 380 nm, where many azobenzene derivatives in the azo form show an absorption band.[2,3] The weakness of all the Raman bands in this spectrum indicates that the quinoid form is the less dominant tautomer at pH 4. In the solution in 1 M HCl, TrO shows strong resonance Raman bands at 1628, 1500, and 1290 cm^{-1} all attributable to the quinoid structure. On deuteration, the first two bands remain unchanged while the last disappears completely just as in case of the acid form of *p*-aminoazobenzene derivatives.[1] TrO in 1 M HCl is therefore described best as the zwitterionic resonance hybrid contributed mainly by the quinoid structure.

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