Physicochemical Properties of Schiff Bases. II.[1] Tautomeric Equilibrium of Substituted *N*-Salicylidene-2-aminopropanes and *p*-Hydroxy-*N*-benzylidene-2-aminopropane

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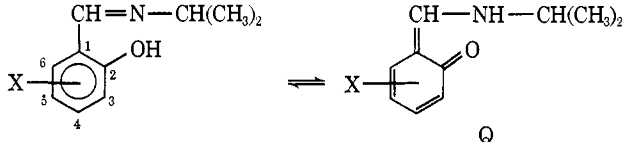
Abstract: The tautomeric equilibrium of substituted *N*-salicylidene-2-aminopropanes and of *p*-hydroxy-*N*-benzylidene-2-aminopropane was studied by ultraviolet and infrared spectroscopy. Additional arguments for the existence of the keto form were provided by the use of the Hammett correlation and by the study of the modifications induced in the infrared spectra by the increase of the amount of water in the solutions. Spectra of the pure keto and enol tautomers were obtained. The equilibrium constants were determined by independent infrared and ultraviolet measurements in a variety of solvents.

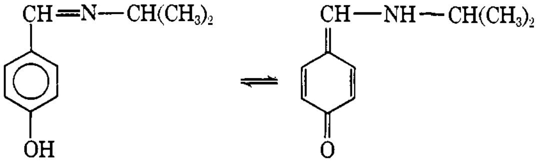
Solvent-induced modifications in the ultraviolet spectra of aromatic Schiff bases have been the subject of several studies.[2] This phenomenon has been related to particularities in the nmr[3] and infrared[4] spectra of these compounds. Generally, it has been attributed[5] to a tautomeric equilibrium between the phenol–imine and the keto–amine forms of the Schiff bases. However, this interpretation has been questioned by some workers.[6] The present study gives additional evidence for the existence of phenolimine–quinoneamine equilibrium in alkyl–aromatic Schiff bases: substituted *N*-salicylidene-2-aminopropanes



P Q

X = H, 4-CH_3, 4-NO_2, 5-OCH_3, 5-Cl, 5-NO_2

and *p*-hydroxy-*N*-benzylidene-2-aminopropane.



P Q

The possibility that detectable changes would appear in the infrared, corresponding to the modifications observed in the ultraviolet spectra, has been questioned.[7] The only known infrared results[4b] were obtained with solvents inducing only small changes in the spectra, so that no quantitative correlation could be made with ultraviolet results. In this study a wide variety of solvents was used. The infrared spectra of the two tautomers are actually quite different if they are recorded in the appropriate solvents. The displacement of equilibrium by variation of the solvent may be followed in the infrared as well as in the ultraviolet. Independent calculations of the equilibrium constants can be made in both cases. They can be compared with the values found by others for similar compounds.[5b,8]

Experimental Section

The Schiff bases were prepared by condensation of commercially available isopropylamine with the appropriate aldehyde, following known procedures.[9] The solvents were infrared grade and were used without further purification, except for dioxane which was dried over molecular sieve.

Ultraviolet spectra were obtained with the Perkin-Elmer Model 350 spectrophotometer and infrared spectra with the Perkin-Elmer Model 225. Variable path length cells with CaF_2 windows were used in the infrared. The cell thickness was in the range of 50 μm and the solution concentrations were around 0.1 *M*. Owing to the hydrolysis of the Schiff bases, it was necessary to extrapolate to zero time the spectra obtained in aqueous solutions.

Dissociation constants of conjugated acids of the free bases and of their anions as well as of the salicylaldehydes were determined from the changes in the ultraviolet absorption curves with pH, as explained in ref 1. In the case of the 4-NO_2 substituted Schiff base, the difference between the spectra of the base and its anion was too small for a precise calculation; the pK_2 was then deduced from the curve giving the variation of the rate of hydrolysis with pH.[10] In all cases where both methods were used, they furnished the same results. The constants were measured at 30° in doubly distilled water containing 2% Spectrograde methanol for solubility. Given values of pK are reliable to within 0.05 pK unit.

Results and Discussion

A way to investigate the tautomeric equilibrium is to try to correlate the observed dissociation con-

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[1] Part I: W. Bruyneel, J. J. Charette and E. de Hoffmann, *J. Amer. Chem. Soc.*, 88, 3808 (1966).

[2] (a) L. N. Fergusson and I. Kelly, *J. Amer. Chem. Soc.*, 73, 3707 (1951); (b) J. Hires and L. Hackl, *Acta Phys. Chem.*, 5, 19 (1959); (c) D. Heinert and A. D. Martell, *J. Amer. Chem. Soc.*, 85, 183 (1963); (d) J. Charette, G. Faltlhansl, and P. Teyssié, *Spectrochim. Acta*, 20, 597 (1964); (e) H. D. Cohen, Y. Hirshberg, and G. M. J. Schmidt, *J. Chem. Soc.*, 2051 (1964).

[3] G. O. Dudek and E. P. Dudek, *J. Amer. Chem. Soc.*, 86, 4283 (1964).

[4] (a) D. Heinert and A. E. Martell, *J. Amer. Chem. Soc.*, 84, 3257 (1962); (b) V. Minkin, O. Osipov, and V. Sheinker, *Russ. J. Phys. Chem.*, 44, 12 (1970).

[5] (a) K. Chatterjee and B. E. Douglas, *Spectrochim. Acta*, 21, 1625 (1965); (b) G. O. Dudek and E. P. Dudek, *J. Amer. Chem. Soc.*, 88, 2407 (1966); (c) G. O. Dudek and E. P. Dudek, *J. Chem. Soc.*, 1376 (1971), and references therein; (d) J. W. Ledbetter, Jr., *J. Phys. Chem.*, 70, 2245 (1966); 71, 2351 (1967); 72, 4111 (1968); (e) M. D. Cohen, G. M. J. Schmidt, and S. Flavian, *J. Chem. Soc.*, 321 (1967).

[6] D. N. Shigorin, I. Pavlenishvili, G. Panova, B. Bolotin, and N. Shapetko, *Russ. J. Phys. Chem.*, 40, 822 (1966).

[7] D. Lexa, M. M. Duval, and R. Viovy, *J. Chim. Phys. Physicochim. Biol.*, 65, 292 (1968).

[8] J. P. Bidegaray and R. Viovy, *J. Chim. Phys. Physicochim. Biol.*, 66, 1479 (1969).

[9] K. N. Campbell, A. H. Sommers, and B. K. Campbell, *J. Amer. Chem. Soc.*, 66, 82 (1944).

[10] Part III, submitted for publication.

stants with the substituent σ values. The various constants are defined as follows.

$$K_T = [Q]/[P] \quad (1)$$

$$K_{1P} = [P][H^+]/[SH^+] \quad (2)$$

$$K_{1Q} = [Q][H^+]/[SH^+] \quad (3)$$

$$K_{2P} = [S^-][H^+]/[P] \quad (4)$$

and

$$K_{2Q} = [S^-][H]^+/[Q] \quad (5)$$

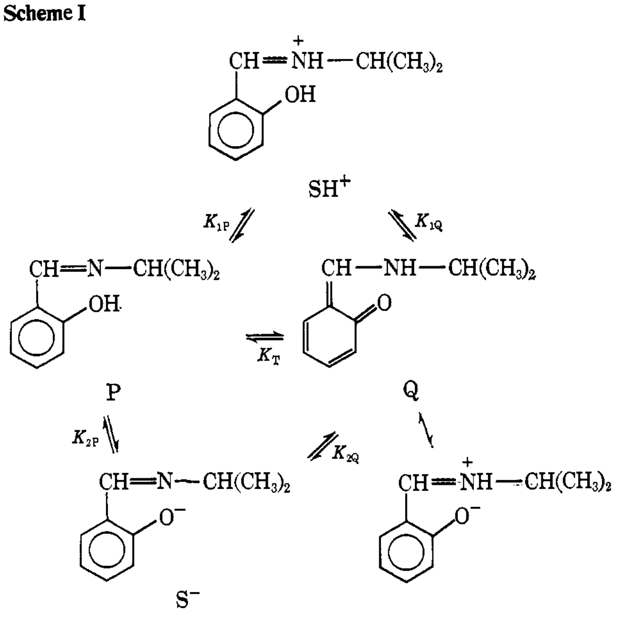
These constants are related to the observed ones by the following equations.

$$K_{1(\mathrm{obsd})} = K_{1P} + K_{1Q} = K_{1P}(1 + K_T) = K_{2Q}(1 + (1/K_T)) \quad (6)$$

$$\frac{1}{K_{2(\mathrm{obsd})}} = \frac{1}{K_{2P}} + \frac{1}{K_{2Q}} = \frac{1}{K_{2P}}(1 + K_T) = \frac{1}{K_{2Q}}\left(1 + \frac{1}{K_T}\right) \quad (7)$$

Scheme I illustrates these correlations. Similar notations apply to the case of *p*-hydroxy-*N*-benzylidene-2-aminopropane. A good Hammett correlation of the observed constants cannot be expected, except in the two limiting cases of a very small or a very large value of K_T. Conversely, a linear correlation will indicate that one of the tautomers is largely in excess. If the protonation occurs at the O site, substituents in the 4 position would be meta and substitutents in the 5 position would be para substituents. The reverse is true if the protonation occurs on the N site. The observed dissociation constants are given in Table I.

Scheme I



In addition to the problem of the magnitude of K_T, the question of the choice of the σ value among the different systems (Hammett,[11] Jaffé,[12] Brown,[13] Taft,[14] Van Bekkum,[15] Yukawa[16]) also arises. We have found the systems of Taft and Van Bekkum equally satisfactory. Taft values are used thereafter unless otherwise stated. In all cases, substituents with strong para resonating power were excluded from the correlation. Their σ_p value has been subsequently calculated from the correlation straight line.

Table I. Dissociation Constants[a] of Substituted Salicylaldehydes (pK) and *N*-Salicylidene-2-aminopropanes (p$K_{1(\mathrm{obsd})}$ and p$K_{2(\mathrm{obsd})}$)

Substituent	pK	p$K_{1(\mathrm{obsd})}$	p$K_{2(\mathrm{obsd})}$
H	8.25	4.70	11.90
4-CH_3	8.42	4.74	12.16 (12.2)[b]
4-NO_2	6.63	2.93	(9.9)[b]
4-OCH_3	8.01		
5-OCH_3	8.40	4.89	11.55 (11.6)[b]
5-Cl	7.45	4.05	11.02 (10.9)[b]
5-NO_2	5.42	2.18	10.03 (10.0)[b]
5-CH_3	8.79		
5-Br	7.51		

[a] In terms of hydrogen ion activity, as obtained from glass electrode measurements. [b] Values given in parentheses were obtained from the kinetic curves.[10]

For the pK_1's of substituted *N*-salicylidene-2-aminopropanes, no correlation was found when the substituents were related to the azomethine site. On the contrary, a good correlation appeared when the protonation was supposed to occur on the carbonyl site of the Q tautomer.

$$\mathrm{p}K_1 = 4.61 - 2.49\sigma^0 \quad (r = 0.99)$$

This may be compared with the dissociation of salicylaldehydes

$$\mathrm{p}K = 8.24 - 2.43\sigma^0 \quad (r = 0.986)$$

and of phenols. For the phenols, the following correlation has been recalculated from published data:[17]

$$\mathrm{p}K = 9.97 - 2.27\sigma^0 \quad (r = 0.997)$$

It may be concluded that the reactive compound is the quinod tautomer present in large excess. It is interesting to note that in this case, the ortho substituent (CHO or $CH{=}N^+HCH(CH_3)_2$) does not change the slope of the correlation line. It may be worth mentioning that the values of $\sigma_{p\text{-}NO_2}$ calculated from the above equations are respectively 1.23 for the phenol, 1.16 for the salicylaldehyde, and 0.97 for the Schiff base. Van Bekkum[15] had already mentioned the fact that the resonance effect of a *p*-NO_2 is not a constant. In this case it increases in the order Schiff base, salicylaldehyde, phenol. This may also be correlated with the increase of the strength of the H bond as measured by the OH vibration frequencies compared with the ones in the unsubstituted corresponding compound (see Figure 1).

The pK_2's of *N*-salicylidene-2-aminopropanes do not correlate with the substituent σ value related to the carbonyl site, but the correlation is good if one considers the azomethine site.

$$\mathrm{p}K_2 = 11.92 - 2.63\sigma^0 \quad (r = 0.997)$$

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(11) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, pp 188–191.

(12) H. H. Jaffé, *Chem. Rev.*, **53**, 229 (1953).

(13) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958).

(14) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(15) H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 78, 815 (1959).

(16) Y. Yukawa, Y. Tuno, and M. Sawada, *Bull. Chem. Soc. Jap.*, **39**, 2274 (1966).

(17) A. T. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

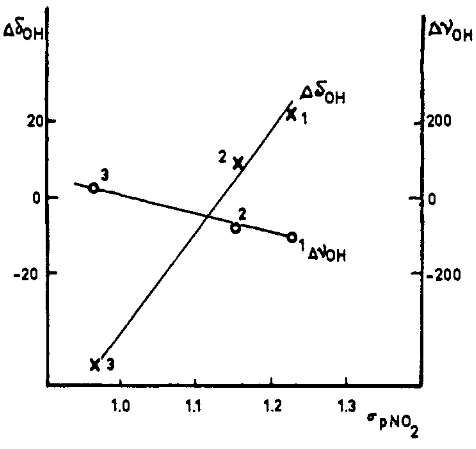

Figure 1. The correlation between the calculated value of σ_p-NO_2 and the displacement of the bonded OH vibrations by introduction of a p-NO_2 substituent: (1) phenol···dioxane; (2) salicylaldehyde, intramolecular bridge; (3) N-salicylidene-2-aminopropane, intramolecular bridge (○, OH stretching; ×, OH bending).

Table II. Values of the Tautomeric Constant K_T and of the Absorptivity of the Q Band in Water–Propanol Mixtures for N-Salicylidene-2-aminopropane

Molar fraction of water	% Q	K_T	a_Q, cm^{-1} l. mol^{-1}
0	9	0.1	8030
0.53	25	0.3	7870
0.63	34	0.5	7770
0.84	47	0.9	7050
0.94	77	3.3	7050
0.997	>81[a]	>4.3[a]	<8137[a]
0.997	94[b]	16[b]	(7050)

[a] These values are higher and lower limits calculated from the residual absorption at 312 μm. [b] These values are calculated from the apparent absorption of the Q band by taking 7050 cm^{-1} l. mol^{-1} for the value of the absorptivity.

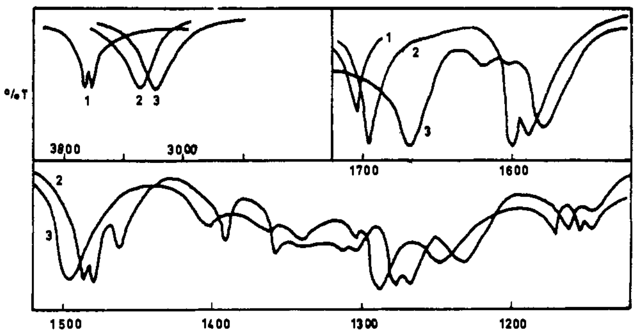

Figure 2. The modification of the infrared spectrum of m-hydroxybenzaldehyde by dissolution in inert solvents: (1) CCl_4; (2) dioxane; (3) KBr disk.

Table III. Characteristic Infrared Bands of the P Form of the Substituted N-Benzylidene-2-aminopropanes[a]

	Substituents					
Vibrations	o-OH	o-OCH_3	m-OH	m-OCH_3	p-OH	p-OCH_3
ν_{OH}	2790		2810		2780	
ν_{CN}	1631	1636	1638	1642	1638	1639
$\nu_{CC(arom)}$	1610	1600		1598	1610	1606
	1581	1581	1591	1582	1589	1578
	1497	1484	1450	1485	1511	1510
δ_{OH}	1278		1290		1282	

[a] All frequencies are given in cm^{-1} for the pure product (film or KBr disk).

This again points to the presence of a largely predominant Q tautomer under the experimental conditions. The amount of both tautomers may be estimated from the relation $K_T = K_{1Q}/K_{1P}$, if it is possible to determine these two dissociation constants. The K_{1P} for the p-hydroxy-N-benzylidene-2-aminopropane should be about equal to the one of the p-methoxy analog (pK_{1P} = 7.1[1]). The observed value for the p-hydroxy is 6.0.[1] Since the difference is more than 1 pK unit, we may admit that this observed value is approximately equal to pK_{1Q}. This leads to a value of about 13 for the tautomeric constant, *i.e.*, 93% of the Q tautomer. Refinement by the use of the Hammett correlation gives 97% from the observed pK_1 and 100% from the observed pK_2. Similar values may be expected for the N-salicylidene-2-aminopropane. A direct determination of the tautomeric constant of this latter compound was made in solvents containing variable proportions of propanol and water. (Propanol was used in order to slow down the hydrolysis reaction.) The band at 312 μm is characteristic of the phenol form (P band). The intensity of this band was taken as a measure of the amount of this tautomer present in the solution. In order to minimize the influence of the variation of the intrinsic intensity with the solvent, the corresponding band was measured for the salicylaldehydes in carbon tetrachloride and in propanol–water mixtures. The intensity of the P band of the Schiff base in propanol–water mixtures was calculated from its intensity in carbon tetrachloride by supposing that its variation with the solvent was the same as for salicylaldehyde. This assumption is borne out by comparison with the o-, m-, and p-methoxy and the m-hydroxy derivatives. The values obtained for the tautomeric constants and for the intensity of the Q band at 400 μm are given in Table II.

Infrared spectra of the Schiff bases were obtained in the same solvents as the ultraviolet spectra. In the pure compounds, as well as in solution in inert solvents, the o-hydroxy and p-hydroxy Schiff bases are in the phenolimine form. This is proven by the similarity of their infrared spectra with the ones of the m-hydroxy Schiff base and of their methoxy analogs, as shown in Table III.

A further confirmation of the proposed structure is furnished by the similarity of the ultraviolet spectra of corresponding hydroxy and methoxy compounds.[1] In order to characterize the hypothetic quinoneamine form of the o- and p-hydroxy Schiff bases, we have observed the modifications in their infrared spectra under the conditions producing the above mentioned modifications in the ultraviolet absorption. It should be noted, however, that large modifications of the infrared spectra may be produced simply by the dissolution process in inert solvents, as may be seen for m-hydroxybenzaldehyde in Figure 2. This is undoubtedly attributable to disassociation by a rupture of the intermolecular H bridge present in the pure compound.[18] The same phenomenon may be ob-

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(18) P. Teyssie and J. J. Charette, *Spectrochim. Acta*, **19**, 1407 (1963).

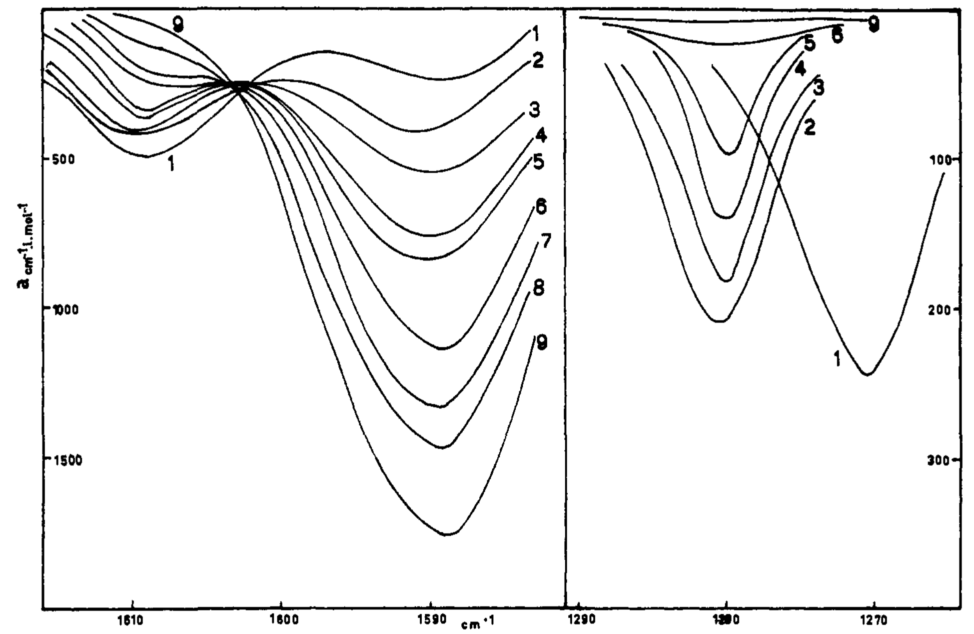

Figure 3. Progressive modifications in the infrared spectrum of *p*-hydroxy-*N*-benzylidene-2-aminopropane in various solvents: (1) dioxane; (2) methanol; (3–8) methanol–water, volume ratio (3) 8/1, (4) 3/1, (5) 2/1, (6) 1/1, (7) 1/2 (8) 1/4; (9) calculated spectrum of the pure Q form.

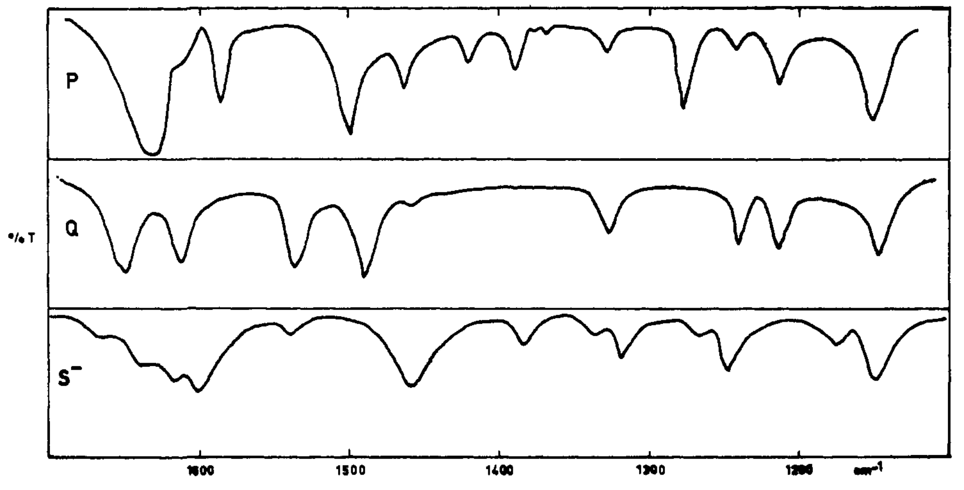

Figure 4. Infrared spectra of the three forms of *N*-salicylidene-2-aminopropane: (P) phenolimine tautomer in dioxane; (Q) quinoneamine tautomer (extrapolated to 100% water); (S^-) anion (solution in CH_3OK).

served in similar compounds, *e.g.*, *m*-nitrophenol and *m*-hydroxy-*N*-benzylidene-2-aminopropane. Similar modifications occur for *p*-hydroxy compounds. In the case of *p*-hydroxy-*N*-benzylidene-2-aminopropane, however, this first modification is followed by a second and progressive one when methanol–water mixtures with an increasing amount of water are used as solvents (see Figure 3). The bands at 1609 and 1278 cm^{-1} disappear; new bands appear at 1590, 1357, 1340, and 1318 cm^{-1}; and the band at 1641 cm^{-1} is replaced by another at 1651 cm^{-1}. These changes may be interpreted by the progressive displacement of the tautomeric equilibrium toward the quinoid form. This displacement results in (1) the disappearance of the OH bending at 1278 cm^{-1} replaced by the NH bending at 1590 cm^{-1}, (2) the replacement of the C=N stretching at 1641 cm^{-1} by the quinoid C=O stretching at 1651 cm^{-1}, and (3) the perturbation of the aromatic bands.

For the *N*-salicylidene-2-aminopropane, there is no modification by dissolution in inert solvents (CCl_4, CS_2, dioxane), the hydrogen bridge being intramolecular. In water–methanol mixtures, however, a new spectrum appears when the amount of water is increased. The OH bending at 1280 cm^{-1} disappears, as well as the aromatic CC at 1582 cm^{-1}; the C=N stretching at 1631 cm^{-1} is replaced by a C=O stretching at 1641 cm^{-1}, and a new band appears at 1533 cm^{-1}, which may be attributed to the amide vinylog NHC=CC=O vibration.[4a] Figures 4 and 5 give the extrapolated (100% water) spectra of the pure Q form. Under the conditions described above, no changes are detectable in the infrared spectra of the corresponding methoxy compounds. We have also verified that the new spectra could not be attributed to the anionic forms of the bases. Spectra of these anions obtained in CH_3OK solutions are included for comparison in Figures 4 and 5.

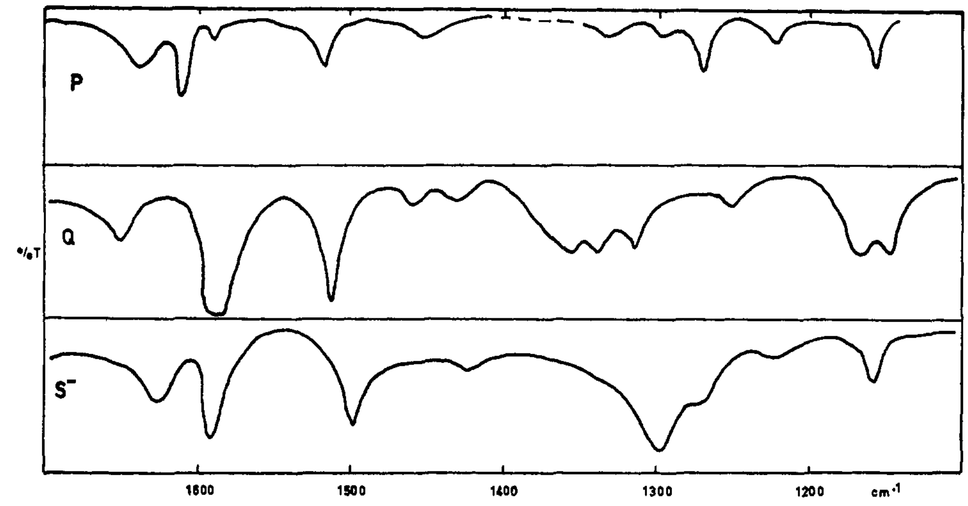

Figure 5. Infrared spectra of the three forms of *p*-hydroxy-*N*-benzylidene-2-aminopropane: (P) phenolimine tautomer in dioxane; (Q) quinoneamine tautomer (extrapolated to 100% water); (S^-) anion (in CH_3OK).

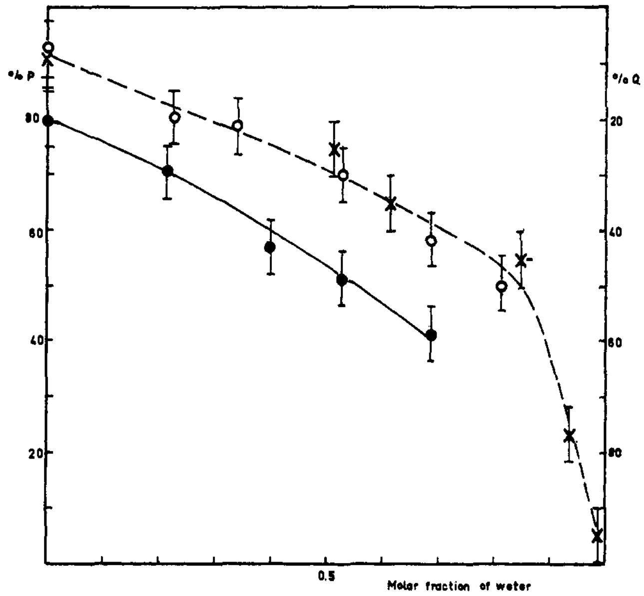

Figure 6. Percentages of the P and Q tautomers of *N*-salicylidene-2-aminopropane in water–methanol (——) and water–propanol (---) mixtures: (×) ultraviolet measurements; (○) infrared measurements.

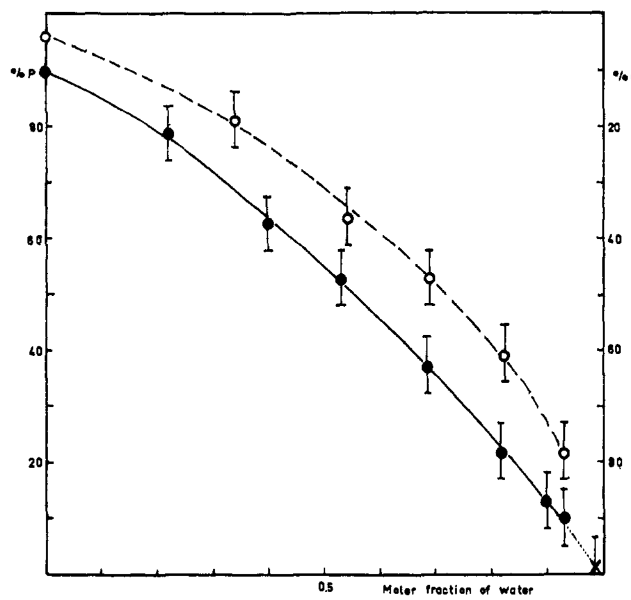

Figure 7. Percentages of the P and Q tautomers of *p*-hydroxy-*N*-benzylidene-2-aminopropane in water–methanol (——) and in water–propanol (---) mixtures: (×) ultraviolet measurements; (○) infrared measurements.

Table IV. Values of the Tautomeric Constants of *N*-Salicylidene-2-aminopropane in Water–Methanol and in Water–Propanol (in parentheses) Mixtures

Vol alcohol/ water	% P calculated from bands at 1582 cm^{-1}	1280 cm^{-1}	1533 cm^{-1}	Mean K_T
1/0	80 (100)	80 (92)	81 (84)	0.25 (0.07)
8/1	71 (83)	71 (76)	72 (83)	0.41 (0.25)
4/1	(86)	(75)	(77)	(0.27)
3/1	56	61	64	0.75
2/1	51 (74)	54 (69)	49 (68)	0.96 (0.43)
1/1	(52)	37 (60)	45 (62)	1.44 (0.72)
1/2			(50)	(1.0)

Table V. Values of the Tautomeric Constants of *p*-Hydroxy-*N*-benzylidene-2-aminopropane in Water–Methanol and in Water–Propanol (in parentheses) Mixtures

Vol alcohol/ water	% P calculated from bands at 1609 cm^{-1}	1278 cm^{-1}	1590 cm^{-1}	Mean K_T
1/0	96 (100)	86 (81)	88 (92)	0.11 (0.04)
8/1	79	79	79	0.27
4/1	(86)	(76)	(80)	(0.23)
3/1	61	63	64	0.59
2/1	54 (46)	46 (70)	58 (63)	0.89 (0.59)
1/1	38 (51)	(60)	37 (49)	1.70 (0.89)
1/2	23 (52)		22 (26)	3.55 (1.56)
1/4			13	6.70
1/6	(22)		10	9.0 (3.52)

Values of the tautomeric constants were obtained in methanol–water and propanol–water mixtures. The intensities of characteristic P bands (1582 and 1280 cm^{-1} for *o*-hydroxy, 1609 and 1278 cm^{-1} for *p*-hydroxy) were calculated from their intensity in dioxane, the ratio of the absorptivities being obtained from the corresponding aldehydes. The mean values of characteristic Q bands (1533 cm^{-1} for *o*-hydroxy, 1590 cm^{-1} for *p*-hydroxy) were obtained from the percentage of Q found above and used to recalculate the constants. Results are given in Tables IV and V and plotted in Figures 6 and 7, with uv results.

Within the experimental errors, the K_T values obtained independently from infrared and ultraviolet measurements are similar. This seems to justify the assumptions made in their calculations. This agreement also supports the contention that the same phenomenon is measured by the two methods. Additional evidence is furnished by the study of the hydrolysis reaction of the Schiff bases under consideration. The rate constants measured by infrared and by ultraviolet, as well as the end product (*i.e.*, the anion of the aldehyde), were the same.

Conclusions

This study warrants the conclusion that the modifications observed in the ultraviolet spectra of *N*-salicylidene-2-aminopropane and of *p*-hydroxy-*N*-benzylidene-2-aminopropane are attributable to a displacement of the keto–enol equilibrium. Some of our results may be compared with the values obtained by Dudek and Dudek[5b] by nmr and by Bidegaray and Viovy[8] by ultraviolet for related compounds. At low temperature in ethanol, Dudek gives a percentage of 14% for the Q form of 2-(*N*-phenylformimidoyl)-phenol. In mixtures of propanol and water, Bidegaray and Viovy have found a curve similar to ours for the variation of K_T *vs.* the amount of water for *N*-salicylidene-1,1-dimethylethylamine. Their value for the absorptivity of the Q form at 387 μm (5900 cm^{-1} l. mol^{-1}) is comparable with the one we have found for *N*-salicylidene-2-aminopropane (7050 cm^{-1} l. mol^{-1}). Determination of the tautomeric constants in various solvents will help to analyze the factors promoting the appearance of the quinoid form. Preliminary measurements already exclude the dielectric constant as a determining factor because the amount of the Q form in dimethylformamide is much less than that in methanol or propanol. The fact that the Q form is largely predominant in water has important consequences for the study of the hydrolysis reaction.[10]

The Redox Behavior of Metallo Octaethylporphyrins

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Abstract: The redox potentials of some 25 representative metalloporphyrins with different central ions have been measured by cyclic voltammetry. In many cases a ligand oxidation–reduction reaction could be discriminated from a metal reaction, through the utilization of visible absorption spectra and esr data. When such data are not available new rules concerning the conformity or nonconformity to redox regularities have been used. It was generally found that central metals are most stable in oxidation states 2+ and 3+ (except for main group IV elements, VO, MoO), and that the reactivity of the porphyrins undergoes substantial variations with different central metals and is determined by the electrostatic action of the central ion. A plot of first reduction *vs.* first oxidation potential of the porphyrin ring yielded a straight line relationship for all of the investigated metalloporphyrins, with the exceptions of Mn^{III}OEP(OH) and MoOOEP(OH). Ag^{III}OEP(ClO$_4$) was found to be stable, and CoOEP was the only compound where the metal could be reduced to the 1+ oxidation state. No special stabilization of low metal oxidation states, as might be expected for a "soft" ligand, was observed. Regularities found in the reduction and oxidation steps of the porphyrin ligand led to the formulation of new "induction parameters" for three- and four-valent metal ions.

Many biological redox systems use metal complexes of soft ligands as reaction centers. Prominent examples of such natural ligands are sulfide in ferredoxin, isoalloxazine in metalloflavoproteins, iron porphyrins in oxidases, cytochromes, and catalases, and magnesium chlorins in the chlorophylls. Highly polarizable ligands can influence the redox potentials and conduction of energy in various systems. The redox behavior of the metal complexes can be widely modified over a large potential range by changing the metal and/or the coordinating ligands. Furthermore, because of their highly conjugated character they are optimally suited for charge transfers to other electron systems. Also, these complexes may undergo addition reactions which may be reversible and serve the purpose of atom transfers (as in the case of flavins) or may be irreversible and serve in the modification or degradation of the ligand (as in the case of bile pigment formation).

During the past several years a number of electrochemical and spectroscopic studies have appeared in both aqueous and nonaqueous media.[2-13] In non-

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(1) (a) Gesellschaft fur Molekularbiologische; (b) Louisiana State University.

(2) A. Stanienda and G. Biebl, *Z. Phys. Chem. (Frankfurt am Main)*, **52**, 254 (1967).

(3) D. W. Clack and N. S. Hush, *J. Amer. Chem. Soc.*, **87**, 4238 (1965).

(4) R. H. Felton and H. Linschitz, *J. Amer. Chem. Soc.*, **88**, 1113 (1966).

(5) (a) J. Manassen and A. Wolberg, *J. Amer. Chem. Soc.*, **92**, 2982 (1970); (b) R. H. Felton, J. Fajer, D. C. Berg, and D. Dolphin, *J. Amer. Chem. Soc.*, **92**, 3451 (1970).