BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3136—3142 (1970)

The Effect of Intramolecular Hydrogen Bonding on the Polarographic Reduction Potentials of Azomethines[1]

Miyoshi UEHARA and Jun-ichi NAKAYA

Department of Chemistry, Faculty of Liberal Arts and Sciences, University of Osaka Prefecture,
Mozu-Umemachi, Sakai-shi, Osaka

(Received January 16, 1969)

The effects of intramolecular hydrogen bonding on the polarographic reduction potentials ($E_{1/2}$) of several azomethines, such as *N*-salicylidenemethylamine, *N,N'*-bis(salicylidene)ethylenediamine, *N*-salicylideneaniline, *N*-salicylidene-*o*-aminophenol, and *N*-benzylidene-*o*-amino-*p*-substituted phenols, have been studied in aqueous and non-aqueous solutions. Contrary to expectations, a larger negative shift of $E_{1/2}$ was observed in the case of *o*-OH-substituted azomethines than in that of unsubstituted azomethines in buffer solutions. On the other hand, the $E_{1/2}$ of the substituted compounds shifted 0.3—0.4V toward the positive side in dimethylformamide or acetonitrile. The relative strengths of hydrogen bonds, as estimated from the positive shifts of $E_{1/2}$, were 6—10 kcal/mol. It has been proposed, from the hydrogen bond strength, the UV spectra, and the *p*-substituent effects, that the introduction of an *o*-OH group into the phenylimino ring provides not a periperpendicular conformation, but a coplanar configuration, by means of the formation of the O–H···N hydrogen bond.

The effects of intramolecular hydrogen bonds due to an *o*-OH substituent on the polarographic reduction potentials indicate a positive shift in contrast to the case with unsubstituted compounds because of the electron-withdrawing character of its substituent. These effects have actually been observed

---

[1] Presented partly at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963 and the 19th Symposium of Polarography, Osaka, Nov., 1967. Paper IV in a series of "Polarography of Azomethine Compounds."

with respect to o-nitrophenol by Astle,[2–4] Page,[5] and Pearson[6] in a buffer solution ($\mathrm{pH}<9$). On the other hand, in the case of salicylaldehyde[7] or o-hydroxyacetophenone,[7] a negative potential shift of 50—70 mV was obtained for $E_{1/2}$, the potential shift by o-OH substituent in this case appears as an electron-donating effect. Doubts regarding the effects of hydrogen bonds on $E_{1/2}$[8] have recently been discussed by Zuman.[9]

We have first investigated polarographically the effects of intramolecular hydrogen bonding with several azomethines in aqueous solutions, in order to interpret the contradictory results for o-OH substituent and unsubstituted azomethines in previous works. It is believed that o-hydroxyazomethines probably form stronger hydrogen bonds than those of nitrophenol and salicylaldehyde because their O–H···N bond is more stable than the O–H···O bond, this is because of their larger polarizable structure between hetero atoms.

Secondly, we investigated the effect of intramolecular hydrogen bonding in an aprotic solvent, such as dimethylformamide (DMF) and acetonitrile (AN). Since the polarographic electrode reduction process of azomethine is accompanied by proton participation,[10] the study of such an aprotic solvent may be useful for estimating the relative strengths of hydrogen bonds.

Lastly, it has been shown that several interpretations can be made on the basis of the findings on hydrogen-bond strengths and UV spectra, especially at the N-side o-OH hydrogen bond of azomethines. If a "periperpendicular conformation[11–13]" can be assumed for N-benzylidene-o-aminophenols, it can be expected that the substituent effect will not appear at the N-side of the –CH=N– bond. These effects on $E_{1/2}$ were investigated in an aprotic solvent.

It can be considered that, together with spectroscopic data such as the IR and NMR data, the polarographic reduction potentials obtained in an aprotic solvent are useful values for studying hydrogen bonds.

Experimental

Materials. The azomethines used as samples were synthesized by the condensation of the corresponding aldehydes and amines in absolute ethanol. The bps and mps of the azomethines used were as follows: (I) N-salicylidenemethylamine bp 229°C, (II) N-benzylidenemethylamine bp 185°C, (III) N,N'-bis(salicylidene)ethylenediamine mp 125—126°C, (IV) N,N'-bis(benzylidene)ethylenediamine mp 53—54°C, (V) N-salicylideneaniline mp 50—51°C, (VI) N-benzylideneaniline mp 52°C, (VII) N-salicylidene-o-aminophenol mp 184—186°C, (VIII) N-benzylidene-o-aminophenol mp 89—90°C, (IX) N-benzylidene-o-amino-p-chlorophenol mp 94.2°C, (X) N-benzylidene-o-amino-p-methylphenol mp 88—88.5°C, (XI) N-(o-methoxybenzylidene)-aniline bp 91°C/5 mmHg, (XII) pyridinealdehyde-(2)-phenylhydrazone(syn-form) mp 88°C, and (XIII) pyridinealdehyde-(2)-phenylhydrazone(anti-form) mp174°C. The other samples, nitro- and aldehyde- compounds, were purified by the distillation or recrystallization of commercial guaranteed reagents. The DMF and AN were purified as has been described by Hatano[14] and by Coetzee[15] respectively. The water content of the DMF, as determined by Karl Fisher titration, was 0.03%.

Apparatus. All the polarograms were obtained by using a Yanagimoto pen-recording polarograph, Model PA-102. The dropping mercury electrode had the following characteristics on an open circuit: a value of $m^{2/3}t^{1/6}=0.99\ \mathrm{mg}^{2/3}\mathrm{sec}^{-1/2}$ was obtained at h=49cmHg in distilled water, or under the same capillary conditions, a value of $m^{2/3}t^{1/6}=1.18\ \mathrm{mg}^{2/3}\mathrm{sec}^{-1/2}$ was obtained in DMF. An aqueous saturated calomel electrode (SCE) was used as the external reference. The electric connection between the SCE and the nonaqueous solution in the polarographic cell was made by means of a DMF-methylcellulose bridge. The IR drop was corrected by measuring the ohmic resistance between the cathode and the anode with a Yokogawa universal bridge, Type BV-Z-13B. All the potentials were corrected with a Shimazu DC potentiometer, Type 3P. The UV spectra were obtained with a Hitachi, Type EPU-2A, spectrophotometer. The pH measurement was done with a Hitachi Model P glass electrode pH meter.

Procedure. The polarographic measurements were carried out with a 0.5 mmol/l depolarizer concentration in DMF or AN in which 0.1 mol/l n-$\mathrm{Bu_4NClO_4}$ had been dissolved or in a Britton-Robinson buffer solution containing 50% ethanol and at a constant temperature of 20±0.5°C.

In a buffer solution, we used a method in which the hydrolysis of azomethines was avoided. Nitrogen was

---

[2] M. J. Astle and W. V. McConell, *J. Amer. Chem. Soc.*, **65**, 35 (1943).

[3] M. J. Astle and W. P. Cropper, *ibid.*, **65**, 2395 (1943).

[4] M. J. Astle and S. P. Stephenson, *ibid.*, **65**, 2399 (1943).

[5] J. E. Page, J. W. Smith and J. G. Waller, *J. Phys. and Colloid Chem.*, **53**, 545 (1949).

[6] J. Pearson, *Trans. Faraday Soc.*, **45**, 199 (1949).

[7] D. M. Coulson, W. R. Crowell and S. K. Tendick, *J. Amer. Chem. Soc.*, **79**, 1354 (1957).

[8] S. F. Dennis, A. S. Powell and M. J. Astle, *ibid.*, **71**, 1484 (1949).

[9] P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N.Y. (1967), p. 94.

[10] L. Holleck and B. Kastening, *Z. Elektrochem.*, **60**, 127 (1956).

[11] N. Ebara, This Bulletin, **33**, 534 (1960).

[12] V. A. Izmailskii and E. A. Smirnov, *Zh. Obshch. Khim.*, **26**, 3042 (1956); *Chem. Abstr.*, **51**, 7145 (1957).

[13] E. Haselbach, E. Heilbronner, *Helv. Chim. Acta*, **51**, 16 (1968).

[14] M. Hatano, T. Yasukawa and M. Yoneyama, *Bull. Chem. Res. Inst. Non-aq. Sol.* (*Tohoku Univ.*), **18**, 155 (1968).

[15] J. F. Coetzee, G. P. Cunningham, D. K. McGuire and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

passed through a base solution of 4.5 m*l* in the polarographic cell in order to remove the dissolved oxygen; to this we then added 0.5 m*l* of a sample stock solution which had previously been deaerated with nitrogen, the polarogram was recorded immediately after the solution had become homogeneous by bubbling in nitrogen.

Results and Discussion

Half-wave Potentials in a Buffer Solution. The half-wave potentials of the first reduction waves on *o*-OH substituted and unsubstituted azomethines were measured in a neutral pH range from 7 to 9, because their hydrolysis rates are large in an acidic medium[16] and because OH substituents dissociate in an alkaline medium.[17] The results are given in Fig. 1. The effect of the *o*-OH group on potentials between *N*-salicylidenemethylamine (I) and *N*-benzylidenemethylamine (II) proved to be a negative shift; this was contrary to the expectation of the positive shift as a result of intramolecular hydrogen bond formation, and the shifted value was 110—120 mV. This value is approximately equal to the negative shift of 90 mV for *p*-hydroxybenzylideneaniline[18] or to that of 120 mV for *p*-hydroxybenzaldehyde.[7] Thus, in the case of (I), the function of the *o*-OH substituent is not electron acceptance but electron donation; similar observations were made in the cases of salicylaldehyde and *o*-hydroxyacetophenone.[7] Most of the similar negative ortho shifts are shown in the data concerning the other compounds in Fig. 1, but in the case of III the reverse shift appears partly at low pH values.

It can be considered that there are two different types of intramolecular hydrogen bonds formed by the *o*-OH substituent. As the half-wave potentials of functional groups, such as $-NO_2$, $>C=O$, and $-CH=N-$, depend upon the hydrogen-ion concentration in an aqueous solution, the participation of a proton which accompanies the electron-transfer process in an electrode double layer should not be ignored. However, the participation of a proton

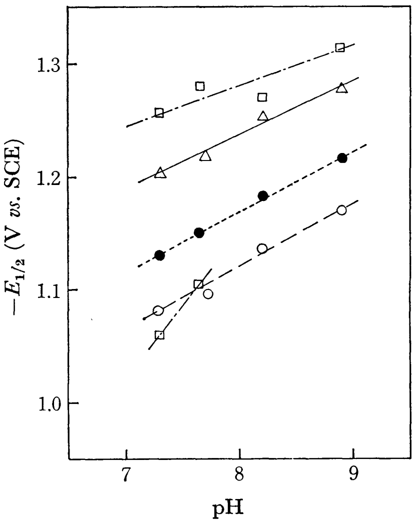


Fig. 1-a. $E_{1/2}$ in buffer solution. Triangle: *N*-salicylidenemethylamine, White Circle: *N*-benzylidenemethylamine, Square: *N*,*N'*-bis(salicylidene)-ethylenediamine, Filled Circle: *N*,*N'*-bis(benzylidene)ethylenediamine.

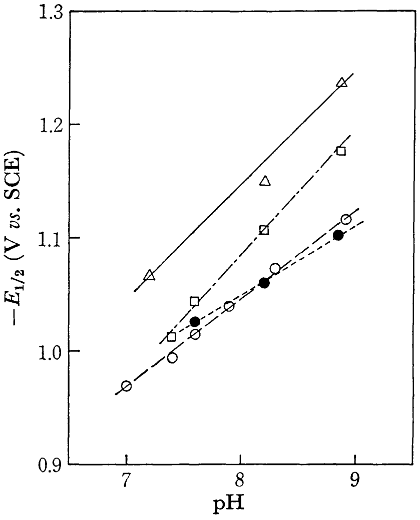


Fig. 1-b. $E_{1/2}$ in buffer solution. Triangle: *N*-salicylideneaniline, White Circle: *N*-benzylideneaniline, Square: *N*-salicylidene-*o*-aminophenol, Filled Circle: *N*-benzylidene-*o*-aminophenol.

TABLE 1. THE EFFECTS OF OH GROUP ON $E_{1/2}$ Sample: 0.5 mmol/*l* in DMF

Compound	$E_{1/2}$ (V *vs.* SCE)	$\Delta E_{1/2}$ *o*-	*m*-	*p*-
$C_6H_5-CH=N-C_6H_5$	−1.90	+0.31*[1]		−0.05
		−0.01*[2]		
		+0.34*[3]		
		+0.32*[4]		
$(C_6H_5-CH=N-CH_2)_2$	−2.27	+0.45		
$C_6H_5-CH=N-CH_3$	−2.27	+0.38		
$C_6H_5-NO_2$	−1.13	+0.25	−0.01	−0.05
C_6H_5-CHO	−1.83	+0.20	+0.01	−0.05
		−0.01*[5]		

The values marked * represent the data in the following substitution.

*[1] *o*-OH on benzylidene
*[2] *o*-OCH_3 on benzylidene
*[3] *o*-OH on phenylimino
*[4] *o*-OH groups on both phenyl rings
*[5] *o*-OCH_3 group on phenyl

---

16) B. Kastening and L. Holleck, *Z. Elektrochem.*, **60**, 130 (1956).

17) R. L. Reeves, *J. Org. Chem.*, **30**, 3129 (1965).

18) M. Uehara, *Nippon Kagaku Zasshi*, **86**, 901 (1965).

in the case of $-NO_2$ may be less active than that of $\rangle C=O$ and $-CH=N-$ because of its stronger resonance effect. Thus, the hydrogen bond in *o*-nitrophenol is probably held in a favorable form for its reduction transition state. On the other hand, it is considered that the hydrogen bond in salicylaldehyde or salicylidenemethylamine is first replaced by proton addition in the diffusion layer and that the *o*-OH substituent acts as an electron donor.

Half-wave Potentials in a Non-aqueous Solvent. The effects of intramolecular hydrogen bonds on polarographic half-wave potentials were investigated under condition in which the potentials could be determined simply by the electron-transfer process. Therefore, the effects of hydrogen bonds on salicylideneamines and also on salicylaldehyde and nitrophenol were observed in DMF, an aprotic solvent, by comparing the difference in $E_{1/2}$'s between *o*-, *m*-, *p*-hydroxy-, or methoxy- substituted and unsubstituted compounds. In Table 1, the $E_{1/2}$ and $\Delta E_{1/2}$ values for these compounds are given, where $\Delta E_{1/2}$ is the difference in $E_{1/2}$ between *o*-, *m*-, and *p*-substituted and unsubstituted compounds. The effects of the *o*-OH substituent on $E_{1/2}$ appear as a uniform positive potential shift in the range of 0.20—0.45 V; this shift is considerably larger than the usual *m*- and *p*- substituent effect on $E_{1/2}$ which has been known in polarography.[18] In the case of the introduction of an OH group into the *m*- or *p*-position, and when it is impossible for a hydrogen bond such as OCH_3 to be formed even in the *o*-position, the negative shift of $E_{1/2}$ takes place because of the effect of their electron donor. The same behavior was observed in the AN (Table 2) used as an aprotic solvent.

TABLE 2. THE EFFECTS OF OH GROUP ON $E_{1/2}$ Sample: 0.5 mmol/*l* in AN

Compound	$E_{1/2}$ (V *vs.* SCE)	$\Delta E_{1/2}$ *o*-	*m*-	*p*-
C_6H_5-CH=N-C_6H_5*	−1.87	+0.31		−0.04
C_6H_5-NO_2	−1.09	+0.23	+0.06	+0.01
C_6H_5-CHO	−1.78	+0.19	−0.01	−0.02

* OH substituent on benzylidene

For most of the compounds investigated in DMF, the polarographic Nernstian slopes (α) were similar to each other concerning the *o*-OH substituted compounds and the unsubstituted ones: $\alpha=62$ mV (*N*-salicylideneaniline), 65 mV (*N*-benzylideneaniline), 58 mV (*N*-salicylidene-*o*-aminophenol), 65 mV (*N*-salicylidenemethylamine), 68 mV (*N*-benzylidenemethylamine), 63 mV (salicylaldehyde), 60 mV (benzaldehyde), 57 mV (*o*-nitrophenol), and 60 mV (nitrobenzene). The above facts suggest that the contribution of the irreversible process in the polarographic reduction may be approximately the same between the *o*-OH substituted compound and the unsubstituted compound. Concerning the polarographic reduction in the aprotic medium, it was expected that $E_{1/2}$ would be determined entirely by the electron-transfer process.

As for the reduction mechanism, it has recently been shown that the azomethines are reduced irreversibly to secondary amines in an aprotic medium through the stage of the formation of free radicals.[19,20] About the half-wave potentials of irreversible systems, the following relationship was derived by Delahay:[21]

$$E_{1/2}=\frac{RT}{\alpha nF}\ln 0.87\, k_f\sqrt{\frac{t}{D}}$$

The reduction mechanism and the values of the transfer coefficient, α, are similar when these compounds are compared, and these substances do not differ substantially in molecular shape or weight. Therefore, the influence of the substituent on the $E_{1/2}$ may be accounted for by the change in the free-activation-energy increment.[22,23]

$$\Delta E_{1/2}\sim\Delta\Delta F^{\pm}$$

The bulk of the azomethine molecules having *o*-OH groups must have been little changed by the formation of the intramolecular hydrogen bond. Therefore, the difference between the entropy change terms ($T\Delta S^{\pm}$) may be neglected compared with that of the enthalpy change ($\Delta H^{\pm}$).
Hence,

$$\Delta E_{1/2}\sim\Delta\Delta H^{\pm}$$

where $\Delta\Delta H^{\pm}$ is regarded as the difference in the lowest vacant MO energy[24] between the hydrogen bonding molecule in the *o*-OH substituted azomethine and the non-hydrogen bonding one. The strengthening of the hydrogen bond due to the electrostatic and mesomeric effects[25] may be considered to result in a lowering of the lowest vacant MO energy. The quite positive shifts of $E_{1/2}$ upon the introduction of an *o*-OH group can be attributed to the decrease in the electron density of the reducible position due to the formation of an intra-

---

19) L. V. Kononenko, V. D. Bezuglyi and V. N. Dmitrieva, *J. Gen. Chem.*, **38**, 2087 (1968); *Zhur Obshch. Khim.*, **38**, 2153 (1968).

20) S. Ono and M. Uehara, *Denki Kagaku*, **27**, 93 (1959).

21) P. Delahay, *J. Amer. Chem. Soc.*, **75**, 1480 (1953), **76**, 5417 (1954).

22) P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y. (1967), p. 25.

23) P. Zuman, *Rev. Polarography*, **11**, 103 (1963).

24) S. Koide, "Polarography," Vol. 3, Nankodo, Tokyo (1965), p. 83.

25) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Translated ed. by M. Ōki, M. Hirota, H. Iwamura and K. Mutai, Tokyo Kagaku Dōjin, Tokyo (1965), p. 128.

molecular hydrogen bond. The facts in Table 1 suggest that the increase in $\Delta E_{1/2}$ may be caused by a strengthening of the hydrogen bond, and the $\Delta E_{1/2}$ is probably related to the relative hydrogen bond strength. Effects other than those of the hydrogen bond in the above case, *i.e.*, the contribution of an inductive effect as a usual electron donor of the OH group, is quite small, as is observed in the case of the $\Delta E_{1/2}$ of the *m*-OH and *o*-OCH_3 groups.

It was confirmed by the invariability of $E_{1/2}$ with the change in sample concentration that the hydrogen bond in this case is not intermolecular, but intramolecular. The invariability of $E_{1/2}$ at varying *N*-salicylideneaniline concentrations is shown in Table 3. In addition, the linear relationship between the concentration of sample and the limiting current seems to show that the diffusion coefficient resulting from the formation of an intermolecular hydrogen bond has not decreased (Table 3).

TABLE 3. INFLUENCE OF CONCENTRATION OF HYDROGEN BONDING MOLECULE ON $E_{1/2}$
Sample: *N*-Salicylideneaniline in DMF

Concn. mmol/*l*	$E_{1/2}$ V *vs.* SCE	i_d μA
0.1	−1.58	0.13
0.2	−1.58	0.25
0.3	−1.58	0.39
0.5	−1.58	0.62
0.7	−1.58	0.90
1.0	−1.57	1.21

Effects of Proton Donors on Half-wave Potentials in a Non-aqueous Solvent. The effects of several proton donors in a non-aqueous solvent on $E_{1/2}$ were investigated in order to study the intramolecular hydrogen bond in detail. When phenol, a proton donor, was added to *N*-benzylideneaniline (VI) in DMF, a new wave (*ba*°) appeared at the (−1.77 V) potential, a little more positive than the half-wave potential (−1.90 V) of the wave (*ba*) of VI (Fig. 2). An increase in the phenol concentration caused the (*ba*°) wave to increase at the expense of the (*ba*) wave. The addition of excess phenol to VI caused the (*ba*) wave to be replaced by the (*ba*°) wave. The effect of the addition of phenol on the reduction of VI may be attributed to the formation of the hydrogen-bonded complex that is reduced at a potential more positive than that of VI (wave (*ba*)). Similar behavior was observed regarding the influence of benzoic acid, as is shown in Fig. 3. However, no such effect of the acid was found with relation to the wave of *N*-salicylideneaniline (V) under the same conditions, and the $E_{1/2}$ (−1.58 V) of V remained constant. It may, therefore, be considered that the intramolecular hydrogen bond of the *o*-OH group in (V) prevents phenol from going close to the nitrogen atom. It seems reasonable to consider that the above facts support the existence and functions of the intramolecular hydrogen bond in V and the intermolecular hydrogen bond be-

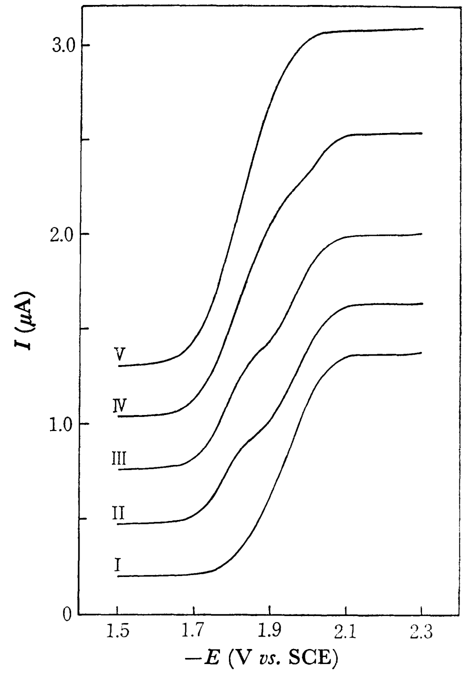


Fig. 2. Influence of phenol on the $E_{1/2}$ of *N*-benzylideneaniline. Sample: 0.5 mmol/*l*. Phenol (mmol/*l*): I) 0; II) 0.1; III) 0.2; IV) 0.5; V) 2.0.

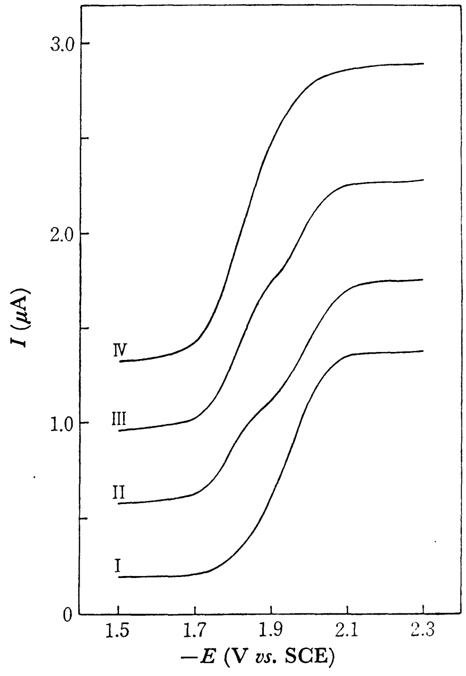
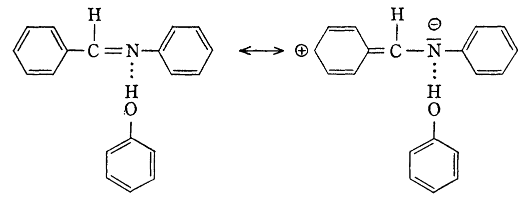
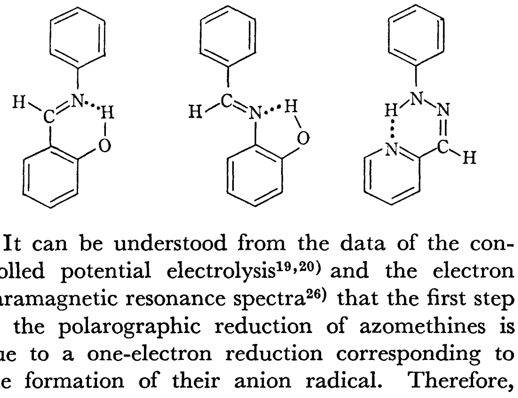


Fig. 3. Influence of benzoic acid on the $E_{1/2}$ of *N*-benzylideneaniline. Sample: 0.5 mmol/*l*. Phenol (mmol/*l*): I) 0; II) 0.1; III) 0.2; IV) 0.5.



tween VI and phenol.

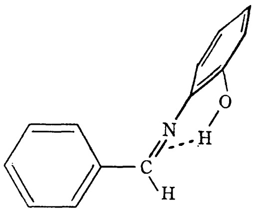
Some Interpretations Regarding the Relative Hydrogen-bond Strength. As has been explained in detail above, the effect of a positive shift of $E_{1/2}$ on several azomethine hydrogen bonds was evaluated to be from 0.31 to 0.45 V. In order to obtain some information on a six-membered ring hydrogen bond for azomethines, the $E_{1/2}$ of pyridinealdehyde-(2)-phenylhydrazone was measured in DMF. As a result it was found that it was -2.03 V for the *anti*-form (XIII) and -1.99 V for the *syn*-form (XII); the shifted values were so small as to be negligible. Thus, the structure required for a positive shifts as the effect of a hydrogen bond seems to be one in which the hydrogen bond is formed adjacent to the polarographic functional group, -CH=N-.



It can be understood from the data of the controlled potential electrolysis[19,20] and the electron paramagnetic resonance spectra[26] that the first step in the polarographic reduction of azomethines is due to a one-electron reduction corresponding to the formation of their anion radical. Therefore, if it is assumed that the $\Delta E_{1/2}$ of *N*-salicylideneaniline obtained from the measurement in DMF is 0.31 eV, the relative strength of the hydrogen bond can be estimated to be 7.1 kcal/mol for this molecule; this agrees with the value of 7 kcal/mol as the mean energy of the O–H···N hydrogen bond.[25] On the other hand, the relative hydrogen bond strength for the *o*-nitrophenol (5.8 kcal/mol), as estimated from the $\Delta E_{1/2}$, agrees with the mean energy, 6 kcal/mol, of the O–H···O hydrogen bond.[25] The relative strengths of the hydrogen bonds obtained from $\Delta E_{1/2}$ can be considered as being appropriate values because they agree with the values in the literature.[25]

Some increase in $\Delta E_{1/2}$ resulted from the introduction of a strong electron-donating substituent into the N-side of such azomethines as *N*-salicylidenealkylamines. It can thus be inferred that the O–H···N hydrogen bond is tightly bound by electrostatic attraction between nitrogen and hydrogen, and that the larger the electron density at N, the larger is the bond energy. The relative strength of the hydrogen bond in *N*-salicylidenemethylamine estimated from $\Delta E_{1/2}$ was about 8.8 kcal/mol.

The strength of the hydrogen bond in *N*-benzylidene-*o*-aminophenol etsimated from $\Delta E_{1/2}$ is much larger than the usual O–H···π hydrogen-bonding energy of 2 kcal/mol.[25] Therefore, it is entirely impossible to suppose an O–H···π hydrogen bond in the molecule; the O–H···N hydrogen bond should be supposed in this case.



Coplanarity of the Molecular Structure due to Hydrogen Bonding. It has been reported in detail that the azomethine molecule exists as a stable non-planar conformation in which the dihedral angle between the N-side phenyl and the rest of the molecule plane is distorted (periperpendicular conformation[11,12]). This interpretation was recently supported by Haselbach *et al.*[13] They showed that the absorption maxima on *trans*-stilbene and on *trans*-azobenzene were situated at wavelengths of about 230 and 320 mμ, while those of *N*-benzylideneaniline were at 262 and 315 mμ in cyclohexane. Moreover those data indicated that the absorption maximum of *N*-benzylideneaniline in concentrated sulfuric acid shifted to the longer wavelength of 340 mμ; this value agreed with that of 3,3-dimethyl-2-phenyl-indolenine. We have also measured some azomethines in absolute ethanol; the results are listed in Table 4.

In the case of *N*-benzylideneaniline (VI), the absorption maximum of the longer wavelengths (306—310 mμ) agrees approximately with the previ-

Table 4. UV spectra of azomethines in absolute ethanol

Azomethines	λ (mμ)	ε ($\times 10^3$)	λ' (mμ)	ε' ($\times 10^3$)
I	253—255	11.6	320—322	3.6
II	244	14.9	280	1.0
III	254—257	21.7	316	8.8
IV	247—248	30.0	280	3.6
V	269	14.3	338	13.1
VI	262	16.9	306—310	8.8
VII	266	10.3	346	11.6
VIII	261	12.8	344	7.2

---

[26] J. M. W. Scott and W. H. Jura, *Can. J. Chem.*, **45**, 2375 (1967).

ous datum (315 mλ) and also with that of *N,N'*-bis(salicylidene)ethylenediamine (III) (316 mμ). It should also be noted that the maximum of the longer wavelength of VI was observed to be 344 mμ in the case of *N*-benzylidene-*o*-aminophenol (VIII). It is possible to give a new interpretation of this compound on the basis of these phenomena; *i.e.*, the two phenyl-rings are probably not distorted because of the hydrogen bond. In this compound, the value of 7.8 kcal/mol estimated to be the relative strength of the hydrogen bond from the $\Delta E_{1/2}$ value of 0.34 eV is slightly larger than that of *N*-salicylideneaniline (V).

TABLE 5. HALF-WAVE POTENTIALS OF *N*-BENZYLIDENE-*o*-AMINO-*p*-SUBSTITUTED PHENOLS IN DMF

Substituent	$E_{1/2}$ (V *vs.* SCE)	$\Delta E_{1/2}$
Cl	-1.45	$+0.11$
H	-1.56	
CH_3	-1.58	-0.02

$\rho=0.30$ V

The effect of *N*-phenyl-substituents on $E_{1/2}$ was investigated for *N*-benzylidene-*o*-aminophenols. As is shown in Table 5, the substituent effect appeared as the potential shift to negative upon the introduction of an electron donor, and as the shift to positive upon the introduction of an electron acceptor. The reaction constant that was obtained from a linear correlation between the reduction potentials and Hammett's substituent constants was 0.30V, similar to those of substituted benzaldehydes (0.31V), benzophenoneoximes (0.30V), stilbenes (0.25V), *etc.* The above results could not be interpreted by periperpendicular conformation. Therefore, the phenyl-ring of the N-side becomes a structure completely co-planar with the rest of the molecular plane, and the effect on $\Delta E_{1/2}$ seems to be one in which a special conjugation effect has been added to the usual hydrogen-bonding effect.

In Table 4, the hypsochromic shifts of the longest wavelength bands upon the introduction of an *o*-OH substituent were obtained with the following values: *N*-salicylideneaniline, 30 mμ; *N*-benzylidene-*o*-aminophenol, 35 mμ; and *N*-salicylidenealkylamines, 36—40 mμ; these values are directly proportional to the relative strengths of the hydrogen bonds of 7.1, 7.8, and 8.8—10.4 kcal respectively as calculated from the polarographic half-wave potentials.

The authors wish to thank Mr. Yasumichi Nakamura for his technical assistance.