Chem. Pharm. Bull.
21(2) 346—352 (1973)

UDC 547.633.4.03.04 : 547.233.04

The Color Reaction in Non-Aqueous Solvents. VI.[1] The Comparison of Tetrabromobenzaurine with Bromophenol Blue in Non-Aqueous Solvents

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(Received August 2, 1972)

We studied in this work the comparison of the reactivity of tetrabromobenzaurine (II) with that of bromophenol blue (I) in methanol–benzene and benzene.

We discussed how the bulky aminated sulfone group in the *ortho* position of I influenced the arrangement of the three phenyls, the approach of anion to a center carbon atom, and the behavior of amines bonded to the phenolic hydroxy group, based on a shift to the longer wave length of II, the fading of II in methanol–benzene, and the comparison of the enthalpies and entropies of the reaction of II with those of I.

It was found that the use of II in the reaction with amines was undoubtedly advantageous over I since an absence of the sulfone group in II resulted in an increase in reactivity of the phenolic hydroxy group with amines and simplification of the reaction.

We discussed in previous papers[3] the reaction of bromophenol blue (I), one of the sulfonephthalein dyes (S.P. dyes), with the tertiary amines in non-aqueous solvents. In these works, we found that I reacts with the tertiary amines in two steps as equation (1) and (2) to yield 1: 1 compounds and 1: 2 compounds and to produce spectral changes in the visible region.

$$H_2A + B \rightleftarrows BH^+\cdot HA^- \qquad [H_2A][B]/[BH^+\cdot HA^-] = K_1 \tag{1}$$

$$BH^+\cdot HA^- + B \rightleftarrows BH^+(BH\cdot A)^- \qquad [BH^+\cdot HA^-][B]/[BH^+(BH\cdot A)^-] = K_2 \tag{2}$$

Where H_2A represents I, and $BH^+\cdot HA^-$ and $BH^+(BH\cdot A)^-$ 1: 1 compounds and 1: 2 compounds, respectively.

Studying these spectral changes, we found the equilibrium constants for the reactions of I with the tertiary amines,[3a] the solvent effects[3b] and the substituent effects[3c] on these reactions. We further reported on the photometric titration of a small quantity of amines with I.[1]

In the second reaction of I with amine (equation (2)), the sulfone group, which acts to make I soluble in water, is not only unnecessary but rather complicates the reaction due to the fact that it is a two-step reaction. It is known that the benzaurine dyes, (B.A. dyes), which are triphenylmethane derivatives, correspond to the desulfonated sulfonephthalein dyes.

Although less frequently used than S.P. dyes due to the fact that they are insoluble in water, the B.A. dyes and aurine dyes (A.R. dyes), which are hydroxy derivatives of the B.A. dyes, are often found in literature.

Based on a series of studies on the B.A. dyes and the A.R. dyes, P. Ramart-Lucas[4] reported on the their spectral and structural changes upon the addition of acids or bases to a variety

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[1] Part V: K. Kigasawa, H. Shimizu, and M. Ibuki, *Yakugaku Zasshi*, **92**, 1009 (1972).

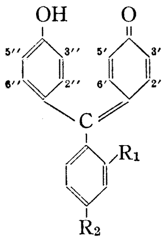
[2] Location: *No. 12-3 Sakurashinmachi-2-chome, Setagaya-ku, Tokyo.*

[3] *a*) K. Kigasawa, Shimizu, and M. Fujino, *Yakugaku Zasshi*, **90**, 380 (1970); *b*) K. Kigasawa, H. Shimizu, M. Fujino, and T. Kohagizawa, *ibid.*, **91**, 1286 (1971); *c*) K. Kigasawa, H. Shimizu, H. Nakaguro, and K. Takeuchi, *ibid.*, **91**, 1292 (1971).

[4] P. Ramart-Lucas, *Bull. Soc. Chim.*, **12**, 477 (1945) [*C.A.*, **40**, 4369 (1946)].

of non-aqueous and aqueous solvents. Ioffe[5] reported the synthesis of many B.A. dye derivatives and the spectral changes in aqueous solution accompanying the changes of pH. Moreover, Hansson[6] studied the equilibrium relations between structurally changed species of B.A. dyes in each pH region by observing the spectral changes and obtained the equilibrium constants and the rate constants for the fading of B.A. dyes. However, we found very little reference related to detailed studies on the spectral changes of B.A. dyes in non-aqueous solvents. Therefore, we investigated the behavior of II in benzene and methanol, based on the assumption that tetrabromobenzaurine (II), which is similar to I in structure, reacts with tertiary amines and furnishes similar spectral changes to those of I.

As the result, we were able to clarify the differences between I and II and the advantageous properties of II over I.



$R_1=SO_3H$, $R_2=H$: sulfonephthaleine
$R_1=R_2=H$: benzaurine
$R_1=H$, $R_2=OH$: aurine

Chart 1

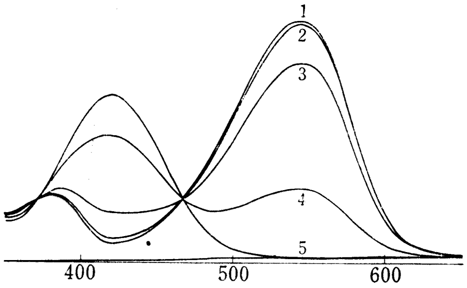


Fig. 1. The Spectral Changes for the Reaction of Tetrabromobenzaurine with Triethylamine at 25°

molar ratio of triethylamine to tetrabromobenzaurine
1. 1000:1 2. 100:1 3. 10:1 4. 1:1
5. 1.6×10^{-5}M tetrabromobenzaurine benzene solution

Result

The Reaction of Tetrabromobenzaurine (II) with Triethylamine

The progressive changes in spectral absorption observed when triethylamine (TEA) is added in successive molar ratio increments (1:1, 10:1, 100:1, and 1000:1) to 1.6×10^{-5}M II benzene solution[7] are illustrated in Fig. 1. The fact that the isosbestic points at 372 mμ and 468 mμ in the spectral changes, which closely resemble those for the reaction of I with TEA, seems to indicate that equilibrium relation between II and TEA is established according to the following equation (1)′. Also we observed that the reactions of II with tertiary amines are similar to the reaction with TEA.

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[5] *a*) I.S. Ioffe, *J. Gen. Chem.* (U.S.S.R.), **17**, 1359 (1947) [*C.A.*, **42**, 2431 (1948)]; *b*) *Idem, ibid.*, **17**, 1370 (1947) [*C.A.*, **42**, 2433 (1948)]; *c*) I.S. Ioffe and Z.I. Pavlova, *ibid.*, **17**, 1688 (1947) [*C.A.*, **42**, 2434 (1948)]; *d*) I.S. Ioffe, *Zhur. Obschei. Khim.*, **17**, 1904 (1947) [*C.A.*, **43**, 5771 (1949)]; *e*) *Idem, ibid.*, **17**, 1916 (1947) [*C.A.*, **43**, 5771 (1949)]; *f*) I.S. Ioffe and Z.I. Pavlova, *ibid.*, **18**, 222 (1948) [*C.A.*, **43**, 5772 (1949)]; *g*) I.S. Ioffe, *ibid.*, **19**, 911 (1949) [*C.A.*, **43**, 8683 (1949)]; *h*) I.S. Ioffe and Z. Ya. Khavin, *ibid.*, **19**, 917 (1949) [*C.A.*, **43**, 8683 (1949)]; *i*) I.S. Ioffe and A.F. Sukhina, *ibid.*, **19**, 1169 (1949) [*C.A.*, **43**, 9451 (1949)]; *j*) I.S. Ioffe and Z. Ya. Khavin, *ibid.*, **20**, 158 (1949) [*C.A.*, **44**, 5593 (1950)]; *k*) I.S. Ioffe, *ibid.*, **20**, 346 (1950) [*C.A.*, **44**, 6130 (1950)]; *l*) *Idem, ibid.*, **20**, 539 (1950) [*C.A.*, **44**, 8661 (1950)].

[6] *a*) H.G. Hansson and O. Nilsson, *Kgl. Fysiograf. Sallskap. Lund. Forh.*, **29**, 91 (1959); *b*) H.G. Hansson, *Acta Chem. Scand.*, **13**, 1309 (1959); *c*) *Idem, ibid.*, **14**, 407 (1960); *d*) H.G. Hansson and O. Nilsson, *Kgl. Fysiograf. Sallskap. Lund, Forh.*, **30**, 27 (1960); *e*) H.G. Hansson, *Acta Chem. Scand.*, **14**, 2021 (1960); *f*) *Idem, ibid.*, **15**, 69 (1961); *g*) *Idem, ibid.*, **17**, 2155 (1963).

[7] Unless otherwise directed, the solution represents the benzene solution.

$$\mathrm{HD} + \mathrm{B} \rightleftarrows \mathrm{B^{+}H \cdot D^{-}} \qquad [\mathrm{B^{+}H \cdot D^{-}}]/[\mathrm{HD}][\mathrm{B}] = K' \qquad (1)'$$

In other words, the original yellow color of the solution, in which only II (HD) is soluble, changes with the addition of TEA or amines (B) in progressive stages through tones of orange to reddish violet which indicates the formation of the 1:1 compounds of II with TEA or amines ($\mathrm{B^{+}H \cdot D^{-}}$).

This reactions are directly affected by the temperature. The reactions proceed to the left proportionate with the rise in temperature, and these reactions are reversible.

Absorption of Tetrabromobenzaurine (II) in Benzene and Methanol Solution

Measurements of the II solution at 418 mμ showed that the molar absorption coefficient is 2.67×10^4 liter/mole and its change at temperature between 25° and 35° is negligible.

Secondly, successive increases in the percentage of methanol to the II benzene solution caused a change in color from yellow through green to violet blue with maximum absorption

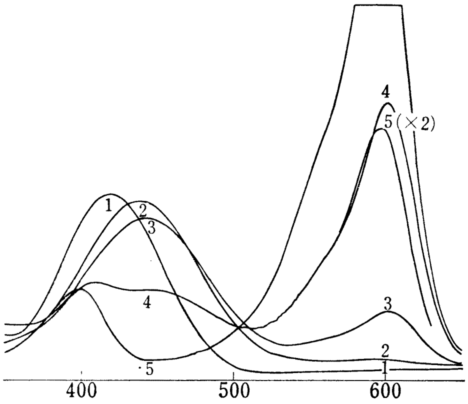

Fig. 2a. The Spectral Changes of Tetrabromobenzaurine (2×10^{-5}M) in Methanol–Benzyene Mixture

1: benzene	4: 50% methanol-benzene
2: 10% methanol-benzene	5: 90% methanol-benzene
3: 20% methanol-benzene	

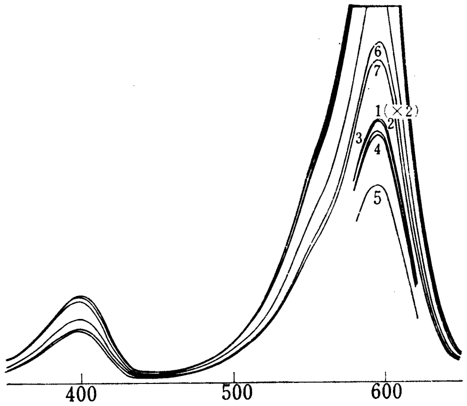

Fig. 2b. The Fading of Tetrabromobenzaurine in the 90% Methanol–Benzene Solution with the Passage of Time

the passage of time

1: 0 hr	2: 1 hr	3: 3 hr	4: 5 hr
5: 24 hr	6: 48 hr	7: 72 hr	

TABLE I. Thermodynamic Constants for the Reaction between Tetrabromobenzaurine or Bromophenol Blue and Tertiary Amines in Benzene

		TEA	TPA	TBA	DMH	DMB	DMP
Tetrabromobenzaurine	$\lambda_{\max}$ (mμ)	546	545	544	541	536	534
	Isosbestic point (mμ)	468 372	467 372	468 372	468 372	464 372	462 372
	log $K'^{a)}$	4.55	3.82	4.01	4.51	2.77	3.44
	ΔH′ (kcal/mole)	−15.9	−15.7	−15.0	−15.5	−12.5	−13.2
	ΔS′ (cal/mole·deg)	−32.6	−35.2	−32.0	−31.3	−29.4	−28.4
Bromophenol Blue	log $K_2^{a)}$	3.98	3.05	3.26	3.98	2.33	2.95
	ΔH (kcal/mole)	−15.4	−15.7	−15.0	$-15.3^{b)}$	$-12.6^{b)}$	$-13.3^{b)}$
	ΔS (cal/mole·deg)	−33.4	−38.7	−35.4	$-33.1^{b)}$	$-31.5^{b)}$	$-31.3^{b)}$
Difference	δ log $K^{c)}$	0.57	0.77	0.75	0.53	0.44	0.49
	$\delta\Delta$H	−0.5	0.0	0.0	−0.2	0.1	0.1
	$\delta\Delta$S	0.8	3.5	3.4	1.8	2.1	2.9

a) at 25° b) K. Kigasawa, H. Shimizu, H. Nakaguro and K. Takeuchi, *Yakugaku Zassi*, **91**, 1292 (1971)

c) $\delta \log K = \log K' - \log K_2$, $\delta\Delta H = \Delta H' - \Delta H$, $\delta\Delta S = \Delta S' - \Delta S$

wave length at 597 mμ. On allowing to stand at room temperature, this color slowly disappeared. On the other hand, the color (blue) of the I methanol solution left standing at room temperature did not disappear appreciably. We recognized this phenomenon to be the difference in the reactivity between I and II.

Thermodynamic Constants in the Reactions of Tetrabromobenzaurine (II) with Tertiary Amines

The equilibrium constants for the reactions of II with the six amines TEA, tripropylamine (TPA), tributylamine (TBA), N,N-dimethylcyclohexylamine (DMH), N,N-dimethylbenzylamine (DMB), N,N-dimethylphenethylamine (DMP) obtained at four arbitrarily selected temperatures between 15° and 45° are presented with the isosbestic points and maximum absorption wave lengths in Table I. The $\Delta H'$ and $\Delta S'$ for the reactions of II with amines were also computed and the differences between $\Delta H'$ and ΔH and between $\Delta S'$ and ΔS were found. Where ΔH and ΔS are the enthalpies and entropies for the reactions of I with the same amines.

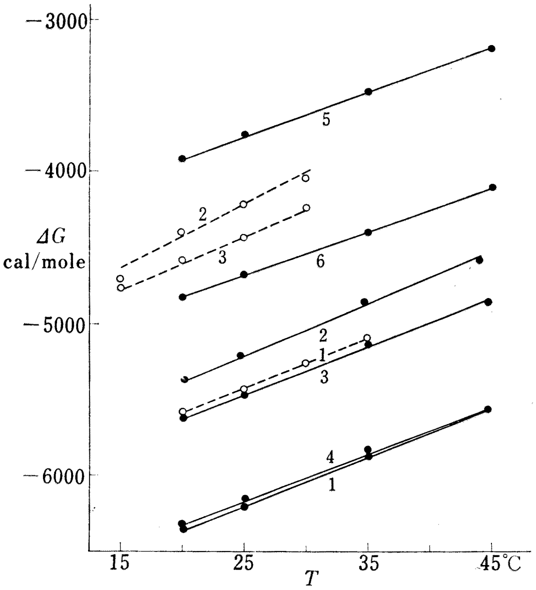

Fig. 3. Plots of Free Energies *vs.* Temperature for the Reaction of Tetrabromobenzaurine (filled circles) or Bromophenol Blue (open circles) with Amines in Benzene

1: TEA; 2: TPA; 3: TBA; 4: DMH; 5: DMB; 6: DMP

Discussion and Conclusion

The Spectra of Tetrabromobenzaurine (II) in Benzene

In benzene, the formation of the 1: 1 compounds of I with amines showed a maximum absorption at 410 mμ, while II showed a shift toward a longer wave length at 418 mμ.

Breslow, *et al.*[8] in their study on the structure of triphenylmethane cation by measurements of ultraviolet (UV) and nuclear magnetic resonance (NMR) spectra, reported that some cations substituted in the *ortho* position have propeller conformation-twisted cations. Klevents, *et al.*[9] also reported that in the N,N-dimethylaniline, the $-N-(CH_3)_2$ group twisted in relation to the ring as groups of progressively larger radii are added in the *ortho* position.

From the above, we believe that in the 1: 1 compounds of I with amines, the twisting of phenyls compelled by the steric hindrance of aminated sulfone group in the *ortho* position obstructs the interaction of 2pπ atomic orbitals of the three phenyls through a central carbon atom which decreases conjugation.[10] However in II, there is less steric hindrance in the *ortho* position than in the 1: 1 compounds of I with amines, so it is thought that the three phenyls remain coplane considerably and the maximum absorption shifts toward a longer wave length in accordance with their conjugation.

Spectra of Tetrabromobenzaurine (II) in Methanol-Benzene Mixture

The addition of methanol to the II solution up to a 90% methanol–benzene solution diminished absorption in the yellow region and produced strong absorption at 597 mμ with a

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[8] R. Breslow, L. Kaplan, and D. LaFollette, *J. Am. Chem. Soc.*, **90**, 4056 (1968).
[9] H.B. Klevens and J.R. Platt, *J. Am. Chem. Soc.*, **71**, 1714 (1949).
[10] Y. Amako, "π Denshi Supekutoru no Riron," Kinokuniya, 1963, pp. 213—222.

blue color. This phenomenon is thought to be attributable to the dissociation of II due to an increase in the dielectric constant through excess methanol and/or the formation of a molecular complex due to the solvation of proton with the lone electron pair on the oxygen atom of methanol.

Secondly, we discussed the fading of II in the 90% methanol–benzene solution. Sager,[11] *et al.* synthesized a variety of S.P. dye derivatives and discussed the effects of the *ortho* and *meta* substituents on the rate constants of the formation of carbinols. They appreciated the steric effects in the *ortho* position, observing that the methyl groups substituted in the *ortho* position reduced the rate constants of the parent S.P. dyes to 1/60—1/100. Moreover, the effects of various substituents in B.A. dyes on the fading were studied by Hansson,[6] and their rate constants were determined spectrometrically. Although it is impossible to compare directly the above-mentioned two experimental data since the experiments by Sager were studied in a 1.12N NaOH aqueous solution and those by Hansson were investigated at less than pH= 11.2, the rate constants which were computed by substituting [OH]=1.12 into the equation by Hansson seem to be several thousand times greater than those for the corresponding S.P. dyes.[12]

Taking the results of the above experiment into consideration, it is readily understandable that the steric hindrance of the aminated sulfone group in the *ortho* position interfered seriously in allowing the methoxy group to approach the center carbon atom and that II is decolorized in methanol–benzene mixture because of the absence of a substituent in the *ortho* position. In other words, the center carbon atom is either highly activated structurally or defficient in electrons enough to react as an acid with methanol.

Molar Absorption Coefficients of 1:1 Compounds of II with Amines

In benzene, the reaction of II with amines can be represented by the equation (1)′. From the fact that the total concentration[13] of II (C_{HD}) is equivalent to the sum concentration of the unreacted II (HD) and the reacted II with amines ($B^+H\cdot D^-$), we can find the equation (4).

$$C_{HD} = [HD] + [B^+H\cdot D^-] \qquad (3)$$

$$= A_1/\varepsilon_1 + A_2/\varepsilon_2$$

$$A_2 = -A_1(\varepsilon_2/\varepsilon_1) + \varepsilon_2\cdot C_{HD} \qquad (4)$$

Where A_1 and A_2 represent absorbances in the yellow and reddish violet regions, ε_1 and ε_2 represent the molar absorption coefficients of II and the 1:1 compounds, respectively.

If we measure A_1 and A_2 when amines in various concentrations are added to the constant concentration of II (2×10^{-5}M) and plot A_1 in abscissa and A_2 in ordinate, a line may be drawn of which the intercept corresponds to $\varepsilon_2 C_{HD}$ and the slope to $-\varepsilon_2/\varepsilon_1$.

In the case of the reaction of I with amines, we have computed ε_1 and ε_2 with the hypothesis, $[H_2A]=0$[14] in the equation (5) when excess amines were added, since the reaction proceeded in two steps.[3a]

$$C_{HA} = [H_2A] + [B^+H\cdot A^-] + [B^+H(BH\cdot A)^-] \qquad (5)$$

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11) E.E. Sager, A.A. Maryott, and M.R. Schooley, *J. Am. Chem. Soc.*, **70**, 732 (1948).

12) S.P. dyes[11] 3′, 3″, 5′, 5″, Br ($k=8.4\times10^{-3}$ min^{-1}. mole^{-1}), 2′, 2″, CH_3, 3′, 3″, 5′, 5″, Br($k=0.8\times10^{-3}$ min^{-1}. mole^{-1}), 3′, 3″, CH_3, 5′, 5″, Br($k=1.87\times10^{-3}$ min^{-1}. mole^{-1}), 2′, 2″, CH_3, 3′, 3″, Br, 5′, 5″, C_3H_7 ($k=0.028\times10^{-3}$ min^{-1}. mole^{-1}). B.A. dyes[6b] 3′, 3″, 5′, 5″, Br($k=1.00\times10^{-2}+41$[OH] min^{-1}. mole^{-1}), 3′, 3″, CH_3, 5′, 5″, Br($k=0.44\times10^{-3}+1.5$ [OH] min^{-1}. mole^{-1}).

13) Concentration: mole/liter.

14) Photometric study in the preceding paper[1] showed the equilibrium constants K_1 for the reaction of I with amines to be $2\times10^8-10^7$ liter/mole. Consequently, hypothesis $H_2A=0$ seemed to be established in previous experiments since the addition of two times concentration of amines to the 2×10^{-5}M I solution yields 99.99% ($K_1=2\times10^8$) 99.88% ($K_1=10^7$) and 98.77% ($K_1=10^6$).

The advantageous point of II over I is that the hypothesis required for I is not necessary and computation of equilibrium constants is much simpler than I.

Absorption in the yellow region is negligible above 520 mμ but absorption in the reddish violet region exists below 418 mμ and contaminates absorption of II. Therefore, we tried to eliminate this contamination in the following way. We took as a corrective factor the ratio of absorbances at 418 mμ to absorbances in the reddish violet region when extreme amounts of amines were added to II (8000 times the molar concentration ratio) and corrected each absorbance at 418 mμ in each concentration.

Moreover, the coloration for this reaction, in contrast to the reaction of II in methanol, was stable.

Equilibrium Constants

From the combination of ε_1 and ε_2 with the equation (1)′, we were able to find the equation (8) for the equilibrium constants.

$$K' = [BH^+D^-]/([HD]([B]-[B^+HD^-])) = (A_2/\varepsilon_2)/((A_1/\varepsilon_1)([B]-A_2/\varepsilon_2)) \qquad (7)$$

$$\log([B]-A_2/\varepsilon_2) = \log(A_2/\varepsilon_2)/(A_1/\varepsilon_1) - \log K' \qquad (8)$$

The intercept of the line, which was drawn by plotting $\log(A_2/\varepsilon_2)/(A_1/\varepsilon_1)$ in abscissa against $\log([B]-A_2/\varepsilon_2)$ in ordinate, corresponds to $\log K'$.

The Comparison of Equilibrium Constants of Tetrabromobenzaurine (II) with Bromophenol Blue (I).

As shown in Table I, the comparison of the reactions of II with amines with those of I indicated that the constants for II were greater than I in all amines.

To elucidate this phenomenon, we calculated, firstly, the enthalpies ($\Delta H'$) and entropies ($\Delta S'$) which contributed to the equilibrium constants.

Nextly, the differences calculated between $\Delta H'$ and ΔH and between $\Delta S'$ and ΔS resulted in −0.5—0.1 kcal/mole and 3.5—0.8 cal/mole. deg., respectively.

Based on the above findings, we might conclude that the energies for the bonding of amines with the phenolic hydroxy group were almost equal[15] but the limiting behavior of amines bonded to the phenolic hydroxy group by the steric interaction with the aminated sulfone group in the *ortho* position of phenyl of I, which is twisted considerably, brought on the decrease in the entropies and this decrease reflected on the differences in the equilibrium constants.

From the above discussion, we may state as follows. To investigate the reaction with amines, II is more advantageous over I since II is strongly bonded to amines, no hypothesis is necessary in calculating the molar absorption coefficient and the equilibrium constants are more easily calculated because II is monobasic acid.

However notice should be taken that in experiments in methanol II progressively changed to carbinol with fading.

Experimental

Instrument——Hitachi Spectrophotometer Model 124. The cell compartment was kept at constant temperature.

Reagents Bromophenol Blue——Prepared as described in the previous paper.[3a)]

Benzaurine——Prepared in accordance with Hansson method[6a)] using benzotrichloride instead of *p*-chlorobenzotrichloride.

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15) M. Kobayashi, M. Fujimoto, and K. Mizumachi, "Kinzoku Kireto Kagobutsu," Kyoritsu, 1960, pp. 124—126.

Tetrabromobenzaurine——Prepared by the bromination of benzaurine in accordance with Meyer method[16] with exception of recrystallization from AcOH. Recrystallization was repeated twice. mp 286° (decomp.). *Anal.* Calcd. for $C_{19}H_{10}O_2Br_4$: C, 38.68; H, 1.71. Found: C, 38.69; H, 1.65.

Benzene——Prepared as described in the previous paper.[3a)]

Methanol——Distilled after boiling with metal magnesium ribbon, twice.

Tertiary Amines——All prepared as described in the previous paper.[3a)]

Molar Absorption Coefficient of Tetrabromobenzaurine——One, 2.0, 3.0, 4.0 and 5.0 ml of the 2×10^{-4}M II soln. were transferred to 25 ml volumetric flasks and diluted with benzene to volume at 25°. The absorbances of the these solutions were determined at 418 mμ at 25°, 30°, 35° respectively. The above procedure was repeated six times.

All measurements led to the correlationship between concentrations (*x*-mole/liter) and absorbances ($-\log T$) as follows.

$$-\log T = 2.67\times10^4 x \quad -0.01 \quad \text{at } 25^\circ$$
$$-\log T = 2.65\times10^4 x \quad -0.01 \quad \text{at } 30^\circ$$
$$-\log T = 2.68\times10^4 x \quad -0.01 \quad \text{at } 35^\circ$$

Spectra of Tetrabromobenzaurine in Methanol—Benzene Mixture——Five 2.5 ml of the 2×10^{-4}M II soln. were transferred to 25 ml volumetric flasks and 2.5, 5, 12.5, 22.5 ml of methanol were added and each soln. was diluted with benzene to volume at 25°, respectively. Spectra of these resulting soln. were drawn from 350 to 650 mμ at 25° (Fig. 2a). Five ml of the 2×10^{-4}M II soln. was transferred to a 50 ml volumetric flask and diluted with methanol to volume and the spectrum of this soln. was drawn from 350 to 650 mμ at 25°. The spectra of the same soln. were drawn at the same condition after allowing to stand for 1, 3, 5, 24, 48, 72 hrs at 25° (Fig. 2b).

Thermodynamic Constants for the Reaction of Tetrabromobenzaurine (II) or Bromophenol Blue (I) with Tertiary Amines——To 5.0 ml of the 2×10^{-4}M II (or I) soln. in six 50 ml volumetric flasks, amines were added in arbitrarily selected six concentrations in accordance with the strength of basicity and diluted with benzene to volume at 25°, respectively. The absorbances A_1 and A_2 of these soln. were measured at 418 mμ (410 for I) and 540—550 mμ at arbitrarily selected four temperatures. In measuring, a period of at least 10 min preceded spectrum recording. Each spectrum was repeated until two successive tracings were identical (to make certain that thermal equilibrium had been reached). ε_1 and ε_2 and K' (K_2) were computed by equations (4), (8) ((5) (2) for I). $\Delta H'$ and $\Delta S'$ (ΔH and ΔS for I) were computed and each equilibrium constant at 25° described in Table I was computed newly from these $\Delta H'$ and $\Delta S'$ (ΔH and ΔS for I).

Acknowledgement We thank Miss A. Kawakami of Tohoku University for elemental analyses.

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[16] R. Meyer and W. Gerloff, *Chem. Ber.*, **57**, 591 (1924).