Studies of the Absorption Spectra of Azo Dyes and their Metal-complexes. II. The Absorption Spectra of Phenolazoacetoacetamide and its Derivatives[*1]

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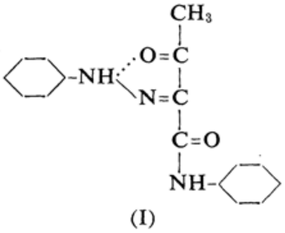
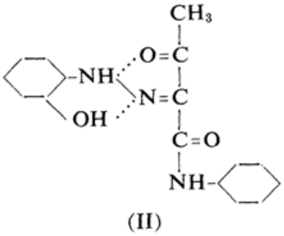
Phenolazoacetoacetamides[*2] can be used as yellow-dyeing metal-complex dyes and have valuable dyeing properties[1]. The relationships between the chemical structure and the absorption spectra of phenolazoacetoacetamides were investigated in this paper.

Results and Discussion

The Chemical Structure of Phenolazoacetoacetanilides and the Assignments of the A and C Bands.—It was concluded in the preceding paper[2] that phenylazoacetoacetanilide (I) and its related compounds have the hydrazone structure and from a hydrogen bond between a carbonyl oxygen and a hydrazone nitrogen atom in the solid state and in non-polar solvents.



(I)



(II)

The infrared spectra of phenylazoacetoacetanilide (I), its 2-hydroxy derivative (II) and 2-methoxy derivative in liquid paraffin are given in Table I. The C=O stretching vibrations of the three compounds are at lower frequencies than those of the strong amide I bands, indicating a marked decrease in frequency compared with ordinary α,β-unsaturated carbonyl systems[3]. Since these frequencies agree with those of phenylazoacetoacetanilide cited in the previous paper, the azo compounds in this paper are also considered to have the hydrazone form. The three compounds show a broad band in the $3000\sim3500\,\mathrm{cm}^{-1}$ region. It is difficult to investigate the exact nature of this band, owing to the superposition of other band systems. In the 2-hydroxy derivative, however, the band is very broad and intense, as is shown in Fig. 1. This band can possibly be attributed to the stretching vibration of the hydroxyl, which forms an intramolecular hydrogen bond

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[*1] Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

[*2] The compounds in this study are named as azo compounds; α-(2-hydroxyphenylazo)-acetoacetanilide, for example, is abbreviated as phenolazoacetoacetanilide.

1) Ciba Ltd., U. S. Pat. 2565898 (1951); Brit. Pat. 716753 (1954); J. R. Geigy A.-G., Brit. Pat., 736034 (1955); E. Koike and Y. Yagi, Japanese Pat. Announced No. 36-8730.

2) Part I, This Bulletin, 36, 487 (1963).

3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", John Wiley & Sons, Inc., New York (1954), p. 153.

TABLE I. INFRARED ABSORPTION SPECTRA OF PHENOLAZOACETOACETANILIDE ETC. (IN SOLID STATE)

Compound	C=O	Amide I	Bands in $3000\sim3500\ \mathrm{cm}^{-1}$
Phenylazoacetoacetanilide	1623 (w)	1667 (s)	3170 (m)
2-Methoxyphenylazoactoacetanilide	1630 (w)	1665 (s)	3170 (w)
2-Hydroxyphenylazoacetoacetanilide	1620 (w)	1640 (s)	3200 (b, s)

w, weak; m, medium; s, strong; b, broad

TABLE II. ELECTRONIC ABSORPTION SPECTRA OF 2-HYDROXY-5-(*N*-ETHYLSULFAMOYL)-PHENYLAZOACETOACETANILIDE

Solvent	A	B	C	D
Standard solvent	387.6 (2.96)	302.6*(0.71)	258.5 (1.85)	231.2 (2.03)
Aqueous 0.01 N NaOH	431.0 (2.20)	323.0*(1.02)	283.3 (2.18)	234.5 (1.96)

Wavelengths (λ) in mμ; Molar extinction coefficients (ε) $\times10^{-4}$ in parenthesis
* Inflection

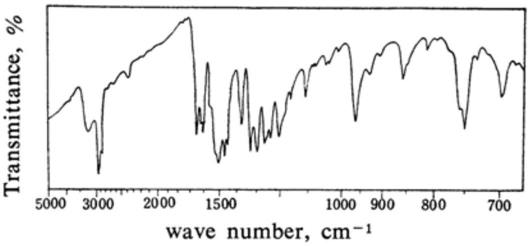


Fig. 1. Infrared absorption spectrum of II (in Nujol mull).

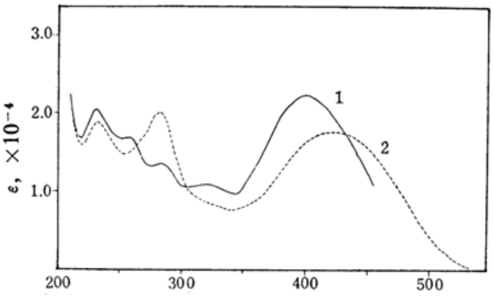
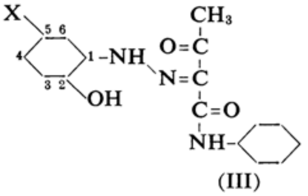


Fig. 2. Absorption spectra of III in anhydrous methanol (1) and 95% methanol (2).

with a hydrazone nitrogen atom, as is shown in II.

The electronic absorption spectra of II in the 200$\sim$500 mμ region show four groups of bands, which will subsequently be referred to as A, B, C and D counting from the longer wavelength side. The absorption spectrum of 2-hydroxy-5-(*N*-ethylsulfamoyl)-phenylazoacetoacetanilide (III) in anhydrous methanol (Fig. 2) shows five bands: D, 232; C, 258 and 281: B, 320; A, 400 mμ. In 95% methanol, however, only four bands (D, 231; C, 282; B, 325 as an inflection; A, 426 mμ) are observed; the band at 258 mμ disappears.



(III)

($X=-SO_2NHC_2H_5$)

The latter spectrum resembles that in an aqueous 0.01 N sodium hydroxide solution (Table II, Fig. 3). In the standard solvent[*3], there is no band at about 280 mμ, and the band C appears distinctly at 258.3 mμ.

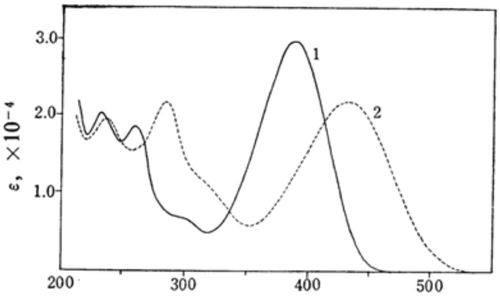


Fig. 3. Absorption spectra of III in the standard solvent (1) and in aqueous 0.01 N NaOH (2).

The above results may be interpreted as follows: The phenolic hydroxyl group is released from the hydrogen-bonded state in polar solvents. This hydroxyl, retaining an equilibrium between a dissociated and an undissociated states in anhydrous methanol (probably due to the absorption of a trace of water while being measured), dissociates in aqueous methanol.

[*3] The term "standard solvent" denotes 80% aqueous methanol containing 0.1 g. of acetic acid per liter.

Table III. Electronic absorption spectra of II and its methoxy-analogue

Compound	Solvent	A	B	C	D
II	S	396.0 (2.81)	(279.0)*(1.00)	258.0 (1.14)	234.0 (1.36)
	H	395.0 (2.59)	319.0* (0.57)	271.0 (1.60) 263.8*(1.48)	243.0*(0.98) 235.7*(1.14) 224.0 (1.20)
Methoxy-analogue of II	S	392.0 (2.88)	277.4* (0.97)	258.5*(1.24)	247.8 (1.33) 237.0 (1.39)
	H	387.4 (2.83)	273.8* (0.95)	253.3 (1.49)	242.5 (1.50) 233.5*(1.43)

Wavelength in parenthesis denotes an indistinct location.
S, Standard solvent; H, *n*-Hexane

The C bands are assigned to a conjugation band (K band)[4] arising from an electronic transition within a partial chromophore[5] consisting of a phenolic nucleus and a hydrazone group. Benzene derivatives usually show B band[6], this band would, however, be submerged by such high intensity K bands as the C bands. Consequently, the absorbing positions and intensities of the C bands alter in accordance with the electronic state of the hydroxyl group. In the standard solvent, the hydroxyl group is fixed in an undissociated state, resulting in a clear-cut formation of the C band.

The A bands are considered to be the absorptions due to a transition involving electron migration along the whole conjugate system of the respective molecule. There also undergo band-shifts according to the polarity of the phenolic hydroxyl, parallel with the shifts of the C bands.

The absorption spectra of II and the 2-methoxy derivative of phenylazoacetoacetamide in the standard solvent and *n*-hexane are shown in Table III. Each band of the 2-methoxy compound in *n*-hexane undergoes a hypsochromic displacement compared with that in the standard solvent. In compound II, λ_{max} of the A band is almost equal in both solvents. However the C band in *n*-hexane is longer in wavelength and higher in intensity than that in the standard solvent, as is shown in Fig. 4. This indicates that the formation of a hydrogen bond ring raises the polar character of the O–H linkage and stabilizes the excited state[7]. Thus, the formation of two internal hydrogen bond rings in a non-polar solvent as shown in II, displaces the A band towards the longer wavelength region.

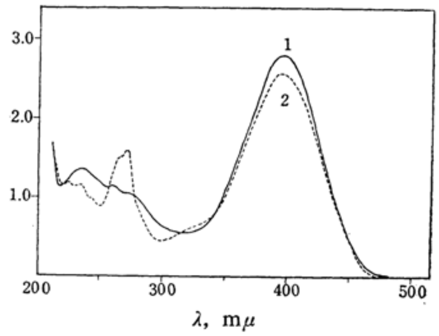


Fig. 4. Absorption spectra of 2-hydroxyphenylazoacetoacetanilide (II) in the standard solvent (1) and in *n*-hexane (2).

It has generally been found[8] that the methylation of a hydroxyl group attached to the conjugate systems causes a small red-shift of the K band. In Table III, however, the A band in both the solvents blue-shifts rather upon methylation. This confirms the view that the hydroxyl group forms the internal or external hydrogen bond in *n*-hexane or in the standard solvent respectively.

The Effects of Substituents in Phenolic Nuclei upon the A and C Bands. — Table IV illustrates the variation of four characteristic bands caused by the introduction of substituents into the phenolic nucleus of II.

The displacements of the C bands by substitution in the 5-position are the most notable and exhibit this decreasing order of λ_{max}: $CH_3 > Cl > H$, $SO_2NH_2 > NO_2$. Such shifts of the C bands suggest that an absorption band due to the electronic transition expected for a partial chromophore is generally very susceptible to the effects of substituents in its chromophore, as has been pointed out by Braude[9]. The maxima of the A bands run

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[4] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy", Edward Arnold Publishers Ltd., Lnodon (1954), p. 111; A. Burawoy, *J. Chem. Soc.*, **1937**, 1865; **1939**, 1177.

[5] E. A. Braude et al., ibid., **1945**, 490; **1947**, 1104.

[6] A. Burawoy et al., ibid., **1955**, 3721.

[7] F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **76**, 1037 (1954); A. Burawoy et al., *J. Chem. Soc.*, **1955**, 3727.

[8] E. A. Braude et al., ibid., **1945**, 498; A. Burawoy et al., ibid., **1952**, 3734.

[9] E. A. Braude, ibid., **1949**, 1902.

TABLE IV. ABSORPTION SPECTRA OF MONOSUBSTITUTED DERIVATIVES OF II IN THE STANDARD SOLVENT

Substituent	A	B	C	D
5-CH_3	401.5 (2.72)	317.0 (0.64)	268.0 (1.14)	231.4 (1.44)
None	396.0 (2.81)	279.0*(1.00)	258.0 (1.14)	234.0 (1.36)
5-Cl	396.0 (2.76)	311.0 (0.68)	262.5 (1.29)	231.5 (1.64)
5-SO_2NH_2	389.5 (2.81)	303.0*(0.63)	258.0 (1.74)	232.5 (1.84)
5-NO_2	391.0 (2.72)	303.0 (1.38)	246.0 (1.56)	231.0 (1.66)
4-SO_2NH_2	394.4 (3.16)	305.6*(0.54)	258.3 (1.37)	231.9 (1.32)
4-NO_2	415.5 (3.94)	325.0 (0.79)	259.8*(1.21)	238.4 (1.46)

TABLE V. SPECTRA OF DISUBSTITUTED DERIVATIVES (IN THE AMIDE PHENYL RING) OF 2-HYDROXY-5-SULFAMOYLPHENYLAZOACETOACETANILIDE IN THE STANDARD SOLVENT

Substituent	A	B	C	D
None	389.5 (2.81)	303.0*(0.63)	258.0 (1.74)	232.5 (1.84)
2-Cl-6-CH_3-	383.5 (2.63)	296.0 (0.56)	254.5 (1.59)	239.0 (1.56)
5-Cl-2-OCH_3-	393.2 (3.09)	300.5*(0.84)	261.0 (1.69)	236.5 (2.38)
2-OCH_3-5-CH_3-	394.0 (2.92)	290.0*(1.03)	259.0 (1.60)	232.5 (2.06)

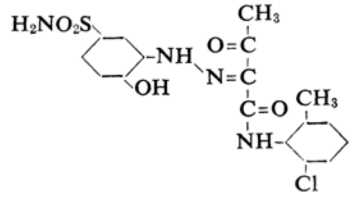
almost parallel with the C bands, though the degrees of displacement are smaller. With regard to sulfamoyl and nitro derivatives in the 4-position, the A bands of both the derivatives are higher in intensity and longer in wavelength than those of corresponding 5-substituted derivatives. However, the λ_{max} values of the C bands are almost equal to that to the non-substituted compound II.

It is interesting that the absorption intensity of the C band in a 5-nitro or 5-sulfamoyl derivative, particularly in the latter, is markedly high.

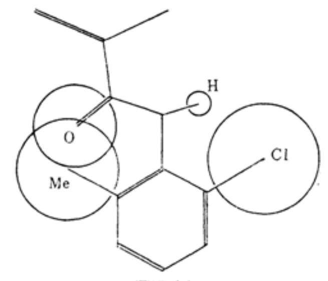
From the results outlined above, it is considered that the substituent in the 5-position—meta to the hydrazone group; i. e., para to the hydroxyl—affects the auxochromic property of the hydroxyl group; e. g., a substitution by methyl emphasizes the auxochromic nature of the hydroxyl group, resulting in the red-shifts of the C and A bands.

On the other hand, the substituent in the 4-position—para to the hydrazone group; i. e., meta to the hydroxyl—is considered to have a mesomeric effect upon the whole absorbing system(10). However this has little effect upon the auxochromic property of the hydroxyl, because the C band undergoes almost no shift upon the introduction of this substituent.

The Steric Inhibition of the π-p Conjugation and the Assignment of the D Bands.—It seems probable that the amide group participates in the origin of the D bands. In 2-hydroxy-5-sulfamoylphenylazoacetoacet-2-chloro-6-methylanilide (IV–a), a steric conformation of the amide-moiety is shown in a projection (IV–b), exhibiting a steric repulsion between the substituent and the carbonyl oxygen. In the above projection, the covalent radius is conveniently taken for the dimension of the methyl and carbonyl radii. Since the covalent radius represents a minimum measure of the interference radii between non-bonded atoms(11), a true overlap would be larger than that in IV-b.



(IV–a)



(IV–b)

N.B. Dimensions used: Bond lengths are Pauling's values(12). H, covalent bond radius 0.31 Å; Me, covalent bond radius 1.39 Å; =O, covalent bond radius 1.10 Å(13); Cl, radius 1.50 Å.

In Table V (Fig. 5), the A, B and C bands blue-shifts with substitution in the 2- and 6-positions are shown. On the other hand, the D

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10) P. H. Gore and O. H. Wheeler, *J. Am. Chem. Soc.*, **78**, 2160, 3363 (1956).

11) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3754.

12) W. Klyne, ed., "Progress in Stereochemistry", Vol. I, Butterworths Sci. Publ., London (1954), p. 361.

13) E. A. Braude et al., *J. Chem. Soc.*, **1949**, 1890.

TABLE VI. VISIBLE BANDS OF MONO-SUBSTITUTED (IN THE AMIDE PHENYL RING) OF 2-HYDROXY-5-SULFAMOYLPHENYLAZOACETOACETANILIDE IN THE STANDARD SOLVENT

Substituent		A
$-OCH_3$	*o-*	392.5 (3.04)
	m-	389.7 (2.94)
	p-	392.0 (2.76)
$-CH_3$	*o-*	388.5 (2.76)
	m-	388.0 (2.53)
	p-	389.5 (2.96)
-Cl	*o-*	390.3 (2.89)
	m-	389.0 (3.02)
	p-	389.5 (3.00)
$-NO_2$	*m-*	388.5 (2.91)
	p-	396.0 (3.52)

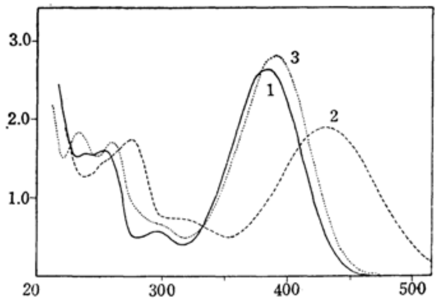
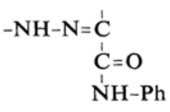


Fig. 5. Absorption spectra of IV-a in the standard solvent (1) and in aqueous 0.01 N NaOH (2). Curve 3 represents the spectrum of 2-hydroxy-5-sulfamoylphenylazoacetoacetanilide in the standard solvent.

band undergoes a reverse shift and a marked intensity-decrease. Consequently, the effect caused by the di-substitution is considered to correspond to Braude's type (2)[14] steric hindrance to uniplanarity; i. e., a phenyl ring within the amide-moiety of the molecule is distorted out of a plane containing -NHCO- and a hydrazone group in the ground state and can not become coplanar or nearly coplanar, even in the excited state. Thus, the A band shows a hypsochromic and a hypochromic displacement, accompanying identical behaviors of the B and C bands.

From the peculiar change of the D band, the following assignment is possible: The D bands are conjugation bands arising from an electronic transition along a partial chromophore V. A phenyl ring within the amide-moiety predominates over a conjugate system involving -NHCO- and the hydrazone group by the π-p conjugation between the phenyl ring and the amide nitrogen atom. When the electronic interaction of the phenyl ring is completely inhibited, these D bands occur in the region of about 240 mμ.



$$\begin{array}{l}-\mathrm{NH{-}N{=}\overset{|}{C}}\\ \qquad\qquad\ \overset{|}{\mathrm{C}}\mathrm{{=}O}\\ \qquad\qquad\ \overset{|}{\mathrm{N}}\mathrm{H{-}Ph}\end{array}$$

(V)

With regard to 2, 5-disubstituted derivatives, e. g., the 5-chloro-2-methoxy compound, it is considered that such disubstitution in the 2- and 5-positions strengthens the π-p conjugation and causes the small hyper- and bathochromic shifts of the D band, resulting in the same displacements of the A band.

The Effects of Substituents (in the Phenyl Ring of the Amide-moiety) upon the A Bands.—On 2-hydroxy-5-sulfamoylphenylazoacetoacetanilide, a variety of substituents was introduced into the phenyl ring of the amide group. The A bands in the standard solvent are shown in Table VI.

As to each substituent, the absorption maxima of *o-* and *p*-derivatives are larger than those of *m*-derivatives. It may be concluded that the substituent exerts a weak mesomeric effect upon the whole absorbing system by the π-p conjugation between the amide nitrogen atom and the phenyl nucleus, resulting in a decrease in the energy of a transition along the system, i. e., λ_{max} increase in the A bands.

Effects of Substituents Adjacent to the Hydroxyl Group upon the Spectra.—The substitution in the 3- or 3, 5-positions in the phenolic nucleus of II is expected to have a marked effect upon the electronic state of the hydroxyl. In Table VII, the A bands mostly split into two peaks. In the case of the $(X, Y=NO_2)$ compound a single A band is located at a fairly long wavelength in the standard solvent and in an aqueous alkaline solution (Fig. 6).

It is considered that the substituent in the 3-position exerts an inductive effect upon the adjacent hydroxyl rather than upon the whole conjugate system; e. g., the introduction of an electron-withdrawing group causes a polarization of the O-H linkage. This is emphasized by the further introduction of such a group in the 5-position. Consequently, the longer wavelength maxima or inflections of the A bands is considered to be due to an electronic transition along the whole conjugate system of the molecule in which the hydroxyl is dissociated. The complete or almost complete disappearance of this band in the

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[14] Cf. Ref. 11; G. M. Gray, ed, "Steric Effects in Conjugated Systems", Butterworths Sci. Publ., London (1958), p. 73.

TABLE VII. SPECTRA OF 3- OR 3,5-SUBSTITUTED DERIVATIVES OF II IN THE STANDARD SOLVENT

Substituent	Sol-vent	A	B	C	D
$3\text{-}NO_2\text{-}5\text{-}H$	S	406.5 (1.87)	355.5*(1.53)	262.7 (1.64)	234.0 (1.60)
	N	472.6 (1.01)	375.8 (0.85)	279.7 (1.12)	236.7 (1.38)
$3\text{-}NO_2\text{-}5\text{-}CH_3$	S	410.0 (1.81)	364.0 (1.66)	265.8 (1.61)	234.5 (1.72)
$3\text{-}NO_2\text{-}5\text{-}Cl$	S	500.0* (0.54), 413.5 (1.68)	350.3 (1.27)	262.5 (1.86)	245.8 (1.96)
	A	410.0 (1.96)	—	—	—
$3\text{-}NO_2\text{-}5\text{-}NO_2$	S	447.5 (2.70)	313.0 (1.30)	273.0 (1.80)	231.6 (1.94)
	N	446.0 (1.96)	366.0 (1.39)	280.0 (1.61)	230.5 (1.77)
	A	(471.0*) (1.00), 410.0 (2.11)	—	—	—
$3\text{-}Cl\text{-}5\text{-}NO_2$	S	471.0* (1.32), 396.0 (2.37)	319.0*(1.32)	270.0*(1.12)	233.0 (1.53)
	N	468.6* (1.50), 415.0 (1.84)	332.0 (0.92)	265.7*(0.92)	242.5*(1.03)
	A	382.0 (2.76)	305.2*(1.21)	247.7 (1.56)	231.6 (1.52)

N, Aqueous 0.01 N NaOH; A, Aqueous 80% methanol containing 0.002 mol. of HCl per liter.

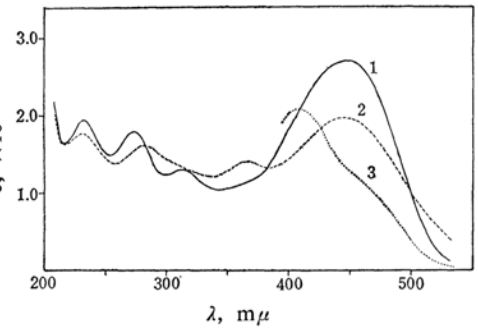
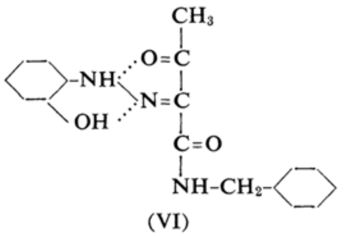


Fig. 6. Absorption spectra of 2-hydroxy-3,5-dinitrophenylazoacetoacetanilide in the standard solvent (1), in aqueous 0.01 N NaOH (2) and in aqueous 80% methanol containing 0.002 mol. of hydrochloric acid per liter (3).

hydrochloric acid-methanol solvent system confirms the above view.

When the splitting of the A band occurs, the C band is located at a longer wavelength than that in the hydrochloric acid-methanol medium and becomes a broad inflection, as is shown in the (X=Cl, Y=NO_2) compound. This is possibly because the molecules of the monoazo compound are in an equilibrium between a dissociated and an undissociated state in this medium.

The Absorption Characteristics of Phenolazoacetoacetbenzylamides and the Assignment of the B Bands. — It has been found[15] that phenolazoacetoacetbenzylamides (VI) form fast-dyeing cobalt(III)-complexes which dye proteinic fibers in clear-yellow shades. It seems reasonable that the four absorption bands in the spectra of phenolazoacetoacetanilides also appear in the series of VI.



(VI)

Further, the C and D bands are expected to approach to and overlap each other, since the π-p conjugation is intercepted by a methylene bridge. In Table VIII, the spectra of phenylazoacetoacetbenzylamide, its 2-hydroxy derivative VI and related compounds are illustrated. The C bands of the former are superposed upon the D band and appear to be a single band. A similar band system is also observed in the spectra of the derivatives of VI (Table IX, Figs. 7 and 8). The spectroscopic behavior of the C band of VI in *n*-hexane is similar to that of II.

The absorption spectra of the 5-substituted derivatives of VI are illustrated in Table IX. The B bands appear more distinctly than those of the II series. The maximum wavelengths of the C bands, as well as those of the A

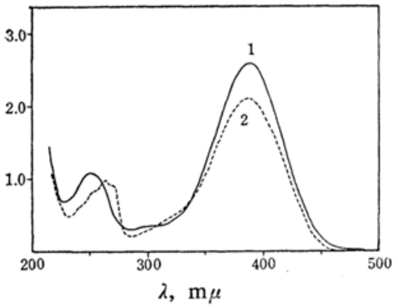


Fig. 7. Phenolazoacetoacetbenzylamide (VI) in the standard solvent (1) and in *n*-hexane (2).

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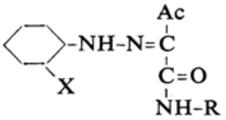
[15] Y. Yagi and K. Kimura, Japanese Pat., Announced No. 36-11975.

TABLE VIII. ELECTRONIC ABSORPTION SPECTRA OF PHENYL- AND PHENOLAZOACETOACETBENZYLAMIDE



X	R	Solvent	A	B	C-D or	
					C	D
H	Benzyl-	S	365.9 (2.67)	287.5 (0.27)	250.8* (1.20) 244.0 (1.33)	
		H	364.6 (2.65)	297.7*(0.30) 288.0 (0.28)	249.2* (1.17) 241.3 (1.37)	
OH	Benzyl-	S	386.8 (2.60)	302.0*(0.34)	(259.7)*(0.95)	249.5 (1.08)
		H	386.1 (2.11)	(310.0) (0.37)	271.5* (0.85) 262.4 (0.98) 253.3* (0.84)	(247.5)*(0.74)
	n-Hexyl-	S	386.1 (2.56)	301.0*(0.31)	259.3* (0.90)	248.7 (1.05)
		H	385.6 (2.13)	—	271.1* (0.90) 261.3 (0.96) 254.9* (0.85)	248.8*(0.75)

TABLE IX. ABSORPTION SPECTRA OF 5-SUBSTITUED DERIVATIVES OF III IN THE STANDARD SOLVENT

Substituent	A	B	C	D
5-$\mathrm{CH_3}$	393.0 (2.46)	308.3*(0.47)	266.5* (0.81)	247.5 (1.02)
None	386.8 (2.60)	302.0*(0.34)	(259.7)*(0.95)	249.5 (1.08)
5-Cl	387.0 (2.42)	306.0 (0.53)	264.0* (0.79)	245.0 (1.15)
5-$\mathrm{SO_2NH_2}$	380.0 (2.60)	296.0 (0.56)	251.7 (1.43)	239.0 (1.43)
5-$\mathrm{NO_2}$	376.0 (2.46)	302.0 (1.18)	246.0 (1.38)	(232.3)*(1.21)

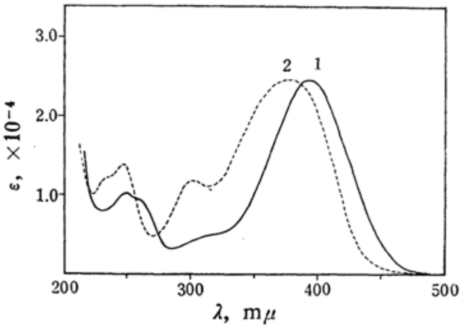


Fig. 8. Absorption spectra of 2-hydroxy-5-methyl- (1) and 2-hydroxy-5-nitrophenylazoacetoacetbenzylamide (2) in the standard solvent.

bands, are displaced towards shorter wavelengths in the order: $\mathrm{CH_3} > \mathrm{Cl} > \mathrm{H} > \mathrm{SO_2NH_2} > \mathrm{NO_2}$. The range of such wavelength variation of the A bands is wider than that in the II series, so suggesting that the electronic transitions along the whole conjugate systems are liable to suffer the effect of the substituent, because the conjugate systems are shorter in this series.

The origin of the B bands has not yet been explored. When X=H in Table VIII, the benzyl derivative shows a very weak B band, one which splits into two peaks in *n*-hexane. This resembles those of such azo compounds as phenylazoacetoacetic acid ethylester in Part I. It has been considered that these bands are due to the n→π transition (R band)[4] of a ketonic carbonyl or of an amide carbonyl, because saturated ketones and α, β-unsaturated ketones usually absorb in the region near 300 mμ[16].

On the other hand, those of the hydroxy derivatives have higher intensities. In Table IX, the more electronegative the substituent in the phenolic nucleus, the higher the intensity of the B band. A similar intensity change was observed in the II series. Table IX also indicates that a compound showing the A band at a relatively longer wavelength similarly exhibits the B band at a longer wavelength position. When measured in an aqueous alkaline solution, both the A and B bands of 2-hydroxy-5-sulfamoylphenylazoacetoacetbenzylamide undergo bathochromic displacement, about 45 and 20 mμ respectively, as compared with those in the standard solvent in Table IX.

If the B bands in the hydroxy derivatives are R bands, they should undergo hypsochromic displacement[4] upon any alteration of the electronic configuration of the system, which

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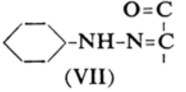
[16] Cf. Ref. 4, pp. 48 and 95.

would cause a bathochromic shift of the K band. Therefore, these bands can not be attributed to the intensified R bands, nor can they be considered to be B bands, because of the high absorption intensities.

1-Phenylazo-2-naphthol[17], 4-phenylazo-1-naphthol[18] and other hydroxyazo compounds[19] are known to exist in a solvent-dependent tautomeric equilibrium between a hydroxyazo- and a *o*-quinonephenylhydrazone form. In such cases, the introduction of an electronegative group into the phenyl ring has been reported to cause an increased contribution of the hydrazone form in equilibrium[17]. It has also been found in 3-methyl-1-phenyl-4-phenylazo-5-pyrazolone as well as in its 2-hydroxyphenylazo-analogue[20], both of which have the hydrazone form, that the greater the Hammett[21] substituent-constant of a substituent in the phenyl ring attached to the hydrazone group, the weaker the hydrogen bond between a carbonyl oxygen and a hydrazone hydrogen atom and, thus, the higher the frequency of the C=O stretching vibration.

Consequently, the B bands are assigned to a conjugation band, which arises from a conjugative transition within a partial chromophore consisting of the acetyl carbonyl and the hydrazone group. The electronegative substituent in the phenyl ring of VII stabilizes the hydrazone form; i. e., it



(VII)

increases the double-bond character of $>C=N-$ and $>C=O$, resulting in the intensity-increase of the B bands. Thus, both 2-hydroxy-5-nitrophenylazoacetoacetanilide and its benzyl analogue exhibit high-intensity B bands in the 302∼303 mμ region.

Experimental

Preparations of 2-Aminophenols.—*2-Amino-4-(N-ethylsulfamoyl)phenol.* — This was obtained in the same manner as were the 4-sulfamoyl derivatives[22], pale gray plates; m. p., 128°C.

Found: C, 44.25; H, 5.38; N, 12.85. Calcd. for $C_8H_{12}O_3N_2S$: C, 44.43; H, 5.59; N, 12.94%.

The other 2-aminophenol derivatives were prepared according to the methods in the literature. Their melting points agree with those in the literature.

Preparation of Acetoacetamides.—*1-Acetoacetylamino-2-methoxy-5-methylbenzene.*—Treatment of *p*-cresidine (m. p. 50.5°C) with diketene in solvent naphtha gave cubic crystals. They were recrystallized from ethanol, giving colorless plates; m. p., 82°C.

Found: C, 65.05; H, 6.69; N, 6.28. Calcd. for $C_{12}H_{15}O_3N$: C, 65.14; H, 6.83; N, 6.33%.

1-Acetoacetylamino-2-chloro-6-methylbenzene.—This was obtained from 2-chloro-6-methylaniline (b. p. 120∼121°C) and diketene. Recrystallization from 50% ethanol gave colorless needles; m. p., 123∼124°C.

Found: C, 58.35; H, 5.05; N, 6.28. Calcd. for $C_{11}H_{12}O_2NCl$: C, 58.53; H, 5.36; N, 6.20%.

Acetoacetbenzylamide. — Colorless plates. Recrystallization from 50% ethanol gave rectangular plates; m. p., 102∼103°C.

Found: C, 68.88; H, 6.72; N, 7.47. Calcd. for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.35%.

Acetoacet-n-hexylamide. — This was obtained as paraffin-like flakes; m. p., 52.0°C.

Found: C, 64.58; H, 10.25; N, 7.25. Calcd. for $C_{10}H_{19}O_2N$: C, 64.90; H, 10.30; N, 7.56%.

The other acetoacetylamino derivatives were obtained in the same manner. The purities were checked by elemental analysis.

Preparations of Phenolazoacetoacetamides. — *2-Methoxyphenylazoacetoacetanilide.* — This was obtained by the treatment of acetoacetanilide with diazotized *o*-anisidine in an aqueous solution. It was recrystallized from ethanol, giving yellow needles.

Found: C, 63.37; H, 5.83; N, 13.65. Calcd. for $C_{17}H_{17}O_3N_3$: C, 65.58; H, 5.50; N, 13.50%.

2-Hydroxy-5-sulfamoylphenylazoacetoacet-2-methoxy-5-methylanilide.—An aqueous solution of diazotized 2-amino-4-sulfamoylphenol was added to a solution containing 1-acetoacetylamino-2-methoxy-5-methylbenzene, sodium carbonate and sodium hydroxide. An orange precipitate was obtained. After an aqueous suspension of this was treated with hydrochloric acid, the precipitate was recrystallized from *n*-butanol, giving yellow needles.

Found: C, 51.49; H, 5.41; N, 13.21. Calcd. for $C_{18}H_{20}O_6N_4S$: C, 51.42; H, 4.80; N, 13.33%.

The Other Phenolazoacetoacetamides.—All of these were synthesized in the above manner. They were recrystallized from ethanol, dioxane, acetoacetic ester, ethylcellosolve or higher alcohols. The purities were checked by elemental analysis.

Measurments of the Absorption Spectra. — Infrared measurements were made by a Shimadzu model IR-27 infrared spectrophotometer equipped with NaCl optics. The Nujol mull method was employed for the preparation of samples. The visible and ultraviolet spectra were measured using a Beckman model DK-2 and a Shimadzu model RS-27 recording spectrophotometers. The spectra were determined at a sufficient dilution, $(0.5\sim2.5)\times10^{-5}$ M, Beer's law being valid within these limits except in hydrous methanol. The solvents used were of spectral grades.

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Summary

Phenolazoacetoacetamides take the hydrazone form. The phenolic hydroxyl group forms an intramolecular hydrogen bond with a hydrazone nitrogen atom in the solid state and in non-polar solvents.

The electronic absorption spectra of these compounds exhibit four groups of characteristic bands: The A bands arise from a transition involving electron migration along the whole conjugate system of the respective compound; the C bands originate in a conjugative electronic transition between a phenolic nucleus and a hydrazone group, and the D bands, in a conjugative electronic transition between a carboxylic acid anilide group and a hydrazone group.

From the investigation of the series of spectra in phenolazoacetoacetbenzylamides, the B bands have been assigned to the conjugation band; they arise from a conjugative electronic transition within a partial chromophore consisting of an acetyl carbonyl and a hydrazone group.

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