

substituent as the result has shown. It is hardly to state what effect(s) due to at the present time. Further investigation such as the reaction conditions and the mechanism by a kinetic method would be necessary for the elucidation of the problem.

Acknowledgement

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The Absorption Spectra of Substituted Azoxybenzenes and the Additivity of their Absorption Maxima

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Azoxybenzene 系化合物들의 分光學的研究 및 그 最大吸收波長의 加成性

韓 治 善

(1962. 8. 30 受理)

Abstract

The ultraviolet and visible absorption spectra of *trans*, *cis*-azoxybenzene, substituted azoxybenzenes and their conjugate acids have been studied. The 320-350m μ main bands of free-base of azoxybenzenes are due to $\pi \rightarrow \pi^*$ transition. These bands of their conjugate acids shown bathochromic shift into visible range. The following empirical relationship between absorption maxima of the main bands was found. $\lambda_{max} = \lambda^{\circ}_{max} + \Delta\lambda_x + \Delta\lambda_y$ This relationship in terms of wave number is also hold in good agreement. $\nu = \nu_0 - (\Delta\nu_x + \Delta\nu_y)$

The ultraviolet and visible absorption spectra of *trans*-azoxybenzene and substituted *trans*-azoxybenzenes have been studied by many workers. Auw-

ers and Heimke¹⁾ seem to have been the first group to have measured the spectra of azoxybenzene and of some of its substitution products. A number of

later workers made more extensive measurements, but added little to the basic understanding of the spectra. Some of the later workers noted the close relation between the spectra of azobenzenes and azoxybenzenes, and very recently a group led by Jaffé² has made real advances in the understanding of azo-compounds and related compounds. They have calculated electron energy-level diagrams by LCAO molecular orbital theory, neglecting overlap integrals, and have used estimates for coulomb and resonance integrals such as to make the calculations as nearly self consistent as possible.³ Based on these calculations, they interpreted the spectra of azobe-

The results of measurements are in reasonable agreement with those of earlier authors, as far as comparable data are available. Since all bands are rather broad, discrepancies of several $m\mu$ between the values reported by different workers reflect the uncertainty in locating the exact absorption peaks rather than any real disagreement between observations. The absorption maxima and extinction coefficients for the compounds observed by the author are summarized in Table I.

The 320-350 $m\mu$ band of azoxybenzenes undoubtedly must represent a $\pi \rightarrow \pi^*$ transition, and in conjugate acid, this band shows a bathochromic shift

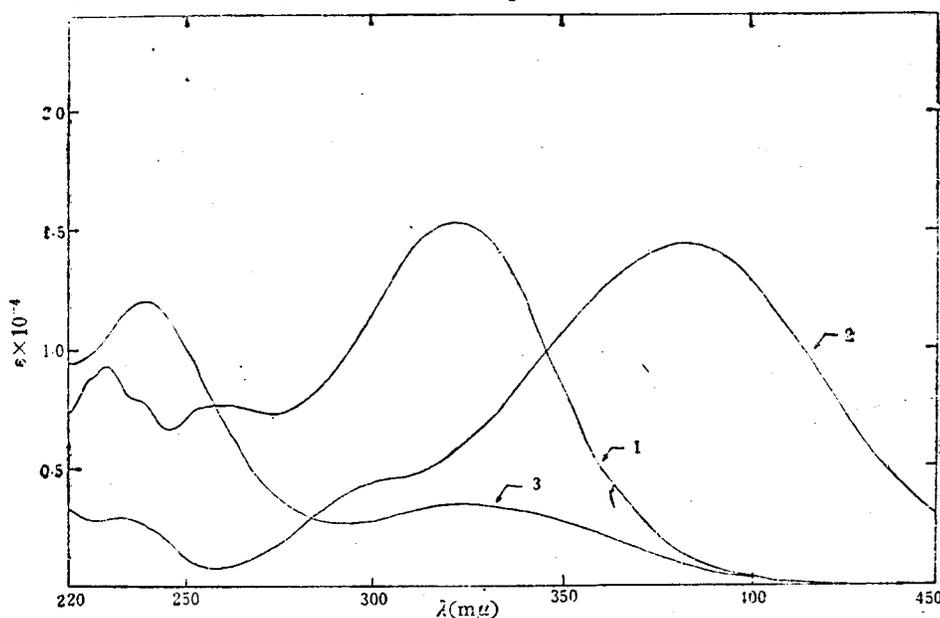


Fig. 1-The spectrum of azoxybenzene.

1. in 95% EtOH. 2. in 20% EtOH-80% H₂SO₄. 3. cis-form in 95% EtOH

nzene in terms of the underlying electronic transitions. Much less work has been done on the interpretation of the spectra of azoxybenzene⁴ and its substitution products. In connection with the investigation of the basicities of mono- and disubstituted azoxybenzenes the spectra of these compounds and of their conjugate acids have been measured.

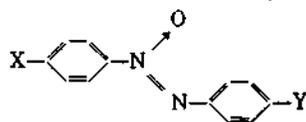
Since the structures of the azo and azoxy groups are similar and have been studied together, the author will discuss the spectra of azoxybenzenes using Jaffé's electron-level diagram.² The spectra of azoxybenzene and its conjugate acid are shown in Fig. 1.

appearing in the region between 390 and 420 $m\mu$.

The most striking difference between the azo- and azoxy-compounds lies in the fact that the $n \rightarrow \pi^*$ transition, observed in azo-compounds at about 440 $m\mu$, and responsible for their color, is absent in azoxy-compounds and their conjugate acids. This is probably due to the tightening effect of the positive charge on the lone pair of electrons surrounding the nitrogen and oxygen atoms, possibly the low intensity $n \rightarrow \pi^*$ transition is submerged in $\pi_1 \rightarrow \pi_1^*$ band.

Besides the main band corresponding to the $\pi_1 \rightarrow \pi_1^*$ transition, another band appeared in the

TABLE I
Absorption Maxima of the Free-Base and It's Conjugated Acid of Azoxy-Compounds



Substituent		Free-Base ⁽¹⁾				Conjugate Acid				Solvent ⁽²⁾
X	Y	$\lambda_{max}(m\mu)$	$\epsilon_{max} \times 10^{-4}$	$\lambda_{max}(m\mu)$	$\epsilon_{max} \times 10^{-4}$	$\lambda_{max}(m\mu)$	$\epsilon_{max} \times 10^{-4}$	$\lambda_{max}(m\mu)$		
1	H H	232	0.94	322	1.55	236	0.62	395	1.22	90% H ₂ SO ₄
2	CH ₃ CH ₃	234	1.07	334	1.79	238	0.55	405	1.73	75
3	Cl Cl	237	0.68	332	1.29	238	0.37	406	1.14	90
4	OCH ₃ OCH ₃	241	0.98	354	2.57	269	1.11	395	3.44	75
5	Br Br	237	1.03	335	2.25	246	0.57	428	2.01	90
6	H CH ₃ (α)	234	0.93	330	1.70	234	—	405	1.69	85
7	CH ₃ H	233	0.99	326	1.71	240	0.32	408	1.70	45
8	H Cl(α)	234	0.91	329	1.74	—	—	391	1.65	85
9	H Br(α)	234	1.06	329	1.82	—	—	394	1.67	85
10	Br H(β)	233	0.97	328	1.79	—	—	390	1.74	85
11	H OC ₂ H ₅	239	0.98	344	1.92	246	0.43	423	2.18	75
12	H OCH ₃	247	1.07	350	2.05	247	0.43	423	2.07	70
13	OCH ₃ H	237	1.01	342	1.91	248	0.60	423	1.96	70
14	H NO ₂	267	1.05	342	1.77	—	—	372	1.50	100
15	CH ₃ Br	238	1.03	334	2.12	—	—	415	1.63	75
16	Br CH ₃	238	1.00	226	2.05	—	—	40	1.98	80
17	OCH ₃ CH ₃	242	1.00	350	2.22	250	0.84	428	2.13	70

⁽¹⁾ 95% EtOH soln.

⁽²⁾ 20 vol.% EtOH—X% H₂SO₄

region around 230-240 m μ . Jaffe²⁾ pointed out that similar bands are observed in the spectra of stilbene (at 220 m μ), benzalaniline (at 220 m μ), azobenzene (at 229 m μ) and phenylnitrene³⁾ (at 227 and 236 m μ). The author noted that the corresponding band of the conjugate acid of azoxybenzenes does not shift very far to the longer wavelength side.

There is only one reasonable explanation of this observation, assuming that the same transition is involved in all these cases. Although the π_1 and π_2^* levels are largely localized on the "vinyl-like" bridge atoms and accordingly the bands are quite sensitive to changes of the coulomb integrals of these atoms, those bands described above are very insensitive to such changes. The energy levels must be separated far enough and are insensitive to changes in the bridge group between rings, since they are comple-

tely localized in the rings. This would suggest that the shorter wavelength side bands correspond to the 'A' \rightarrow 'H' transition such as Platt proposed.⁵⁾

The spectrum of *cis*-azoxybenzene is not reported in the literature. In order to elucidate the structure of *cis*-azoxybenzene, the author have studied its spectrum, which is shown in Fig. 1. In a comparison of the spectra of *trans*- and *cis*-azoxybenzene, we can see a very interesting fact. The $\lambda = 328$ m μ in the spectrum of *cis*-azoxybenzene corresponding to the $\lambda_{max} = 322$ m μ in the spectrum of the *trans*-form is due to the $\pi_1 \rightarrow \pi_1^*$ transition. The intensity of $\lambda_{max} = 328$ m μ of *cis*-azoxybenzene is much less than that of the corresponding band of *trans*-azoxybenzene; whereas, the intensity of the band of $\lambda_{max} = 240$ m μ of *cis*-azoxybenzene is much greater than that of the corresponding band

of *trans*-azoxybenzene.

The reason that a hypochromic effect is observed with *cis*-azoxybenzene at the 328m μ band and a hyperchromic effect at the 240 m μ band can be explained as follows. As we can easily see from the following conformational pictures, the distance between the two benzen rings in the *cis*-form is much closer than that of the *trans*-form. Accordingly the steric hindrance due to the crowding of atoms in the molecule of the *cis*-form is more severe com-

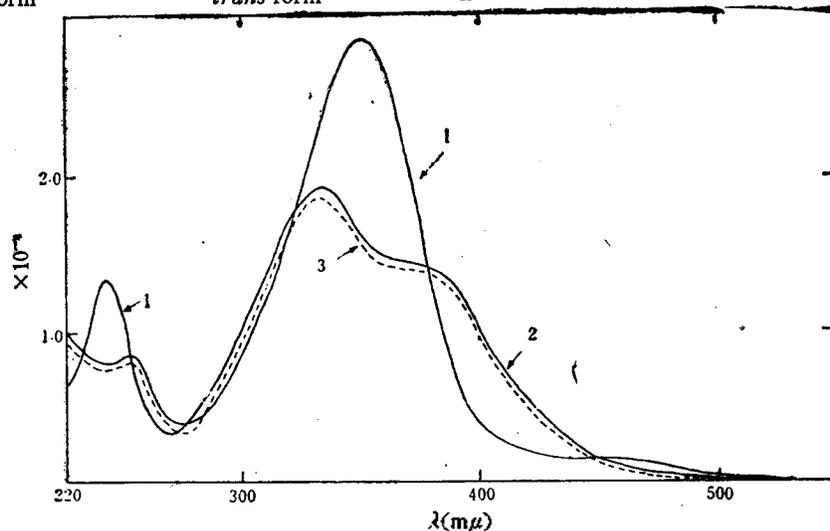
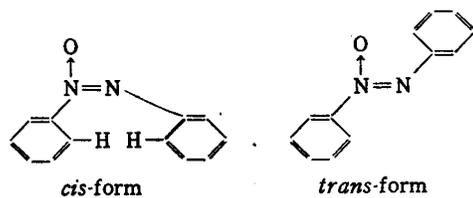


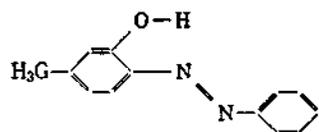
Fig. 2—Absorption spectra of 1. 4-Hydroxy-4-methylazobenzene in 95% EtOH 2. 2-Hydroxy-4-methylazobenzene in 95% EtOH 3. α -Hydroxy-4-methylazobenzene, hydrolyzed from 2- α -Acetoxy-4-methylazobenzene, in 95% EtOH

pared to that of the *trans*-form.^{7,8)} This increased degree of crowding in the *cis*-azoxybenzene must result in the destruction of the coplanarity of the two benzene rings. The hypo and hyperchromic effect in the case of *cis*-azoxybenzene seems to be due to such slight or moderate crowding in the molecule. The author also has tried to obtain the spectrum of the conjugate acid of *cis*-azoxybenzene in sulfuric acid solution. However, it was found that *cis*-azoxybenzene is almost completely converted to its *trans*-form, even with 15 wt. % H₂SO₄.

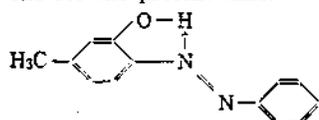
The U.V. spectrum of 2-hydroxy-4-methylazoben-

zene, (2-2), is shown Fig. 2. with that of hydroxy-methylazobenzene. By comparing the two spectra, some interesting facts were observed. In general the $n \rightarrow \pi^*$ electronic transition of *m*- and *p*-substituted azobenzenes appear in the region between 400 and 470 m μ . In the case of *o*-substituted 2-hydroxy-4-methyl-azobenzene, however, the $n \rightarrow \pi^*$ transition band shifted to shorter wavelength side, 372 m μ , and its intensity was increased several times compared to that of $n \rightarrow \pi^*$ band of *p*-substituted azobenzene. In addition to this, the $\pi \rightarrow \pi^*$ transition band of the *o*-substituted azobenzene again shows a significant hypochromic shift, whereas its intensity was decreased considerably. The hypochromic shift of both transitions, the hyperchromic effect of $n \rightarrow \pi^*$ band and the hypochromic effect of $\pi \rightarrow \pi^*$

band of the 2-hydroxy-4-methylazobenzene compared to the *p*-substituted isomer seems to be due to the steric hindrance of *ortho*-isomer. That is, the close distance between the hydrogen atom of hydroxy group and nitrogen atom of azo group may cause the interaction of two atoms, which will distort the coplanarity of two benzene nuclei. This steric hindered non-planarity may be the reason for those spectral facts. There can be another possible explanation for such phenomena. That is, the adjacent hydrogen and nitrogen atom may be bound as hydrogen bond. Thus, the lone pair electrons in the



nitrogen atom, which cause the $n \rightarrow \pi^*$ transition, can not be easily excited to π^* energy level. The π electrons in azo-group, then, will be polarized, which may cause the blue shift and the hypochromic effect of $\pi \rightarrow \pi^*$ band of the *o*-substituted azobenzene. However, it can be hardly concluded that which one of above two explanation is the correct one for the present time.

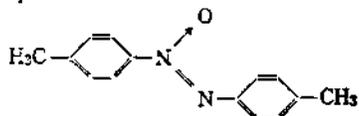


The author found an interesting relationship between the λ_{max} of mono- and disubstituted azoxybenzenes and the λ_{max} of azoxybenzene. This relationship holds only for the main band which corresponds to the $\pi_1 \rightarrow \pi_1^*$ electronic transition. That is,

$$\lambda_{max} = \lambda_{max}^0 + \Delta\lambda_x + \Delta\lambda_y \quad (1)$$

where λ_{max} is the wavelength at which the absorption maximum of the disubstituted azoxybenzene in question appears and λ_{max}^0 is that of the azoxybenzene. The $\Delta\lambda_x$ is the difference of λ_{max} between 4-mono-substituted azoxybenzene and azoxybenzene, and $\Delta\lambda_y$ is that for the 4'-mono-substituted and azoxybenzene.

It is convenient to understand this relationship with an example.

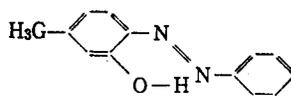


Thus 4,4'-dimethylazoxybenzene is the case of X = CH₃ and Y = CH₃. The $\Delta\lambda_x$ can be obtained from the λ_{max} of 4-methylazoxybenzene and of azoxybenzene, and the $\Delta\lambda_y$ can also be calculated in a similar manner from the λ_{max} of 4'-methylazoxybenzene and azoxybenzene as follows.

$$\begin{aligned} \Delta\lambda_x &= \lambda_{max} \text{ of 4-methylazoxybenzene} - \lambda_{max}^0 \\ &= 326 \text{ m}\mu - 322 \text{ m}\mu \\ &= 4 \text{ m}\mu. \end{aligned}$$

$$\begin{aligned} \Delta\lambda_y &= \lambda_{max} \text{ of 4'-methylazoxybenzene} - \lambda_{max}^0 \\ &= 323 \text{ m}\mu - 302 \text{ m}\mu \\ &= 21 \text{ m}\mu. \end{aligned}$$

Substituting these values into the above equation, the λ_{max} of 4,4'-dimethylazoxybenzene can be obtained



by using the above relationship without experimental observation. This is,

$$\lambda_{max} = 322 + 4 + 8 = 334 \text{ m}\mu.$$

Comparing the calculated λ_{max} with observed λ_{max} (334 m μ , cf. Table I), we can see these two values are in surprisingly good agreement.

The coincidence of the observed λ_{max} and the λ_{max} calculated from the above relationship is acceptable within an error of 1-2 m μ for all the azoxybenzenes investigated with the exception of those involving a OCH₃ group. In the case of the OCH₃ group, the discrepancy of the calculated λ_{max} from the observed one is considerably larger. It is likely that the relation also breaks down for other substituents causing large spectral effects.

Application of the relationship works not only for symmetrically substituted azoxybenzenes but also for unsymmetrically substituted azoxybenzenes. Such agreements are shown in Table II.

The significance of the proposed equation is that we can estimate λ_{max} of symmetrically and unsymmetrically disubstituted azoxybenzenes from the λ_{max} of the related monosubstituted azoxybenzene without experimental observations, and in addition the λ_{max} of a monosubstituted azoxybenzene can be calculated from λ_{max} of the related disubstituted azoxybenzene and λ_{max} of the remaining monosubstituted azoxybenzene.

TABLE I

The Comparison of the Observed λ_{max} and Calculated λ_{max} . Using the Additive Equation

X	Y	$\Delta\lambda^*$	$\Delta\lambda_y$	Max. Calcd. m μ	Max. Obsd. m μ
CH ₃	H	4			
H	CH ₃		8		
CH ₃	CH ₃			334	334
Br	H	6			
H	Br		7		
Br	Br			335	335
CH ₃	H	4			
H	Br		7		
CH ₃	Br			333	334
Br	H	6			

H	CH ₃	8		
Br	CH ₃		336	336
CCH ₃	H	4		
H	CH ₃	28		
OCH ₃	CH ₃		354	350
OCH ₃	H	20		
H	OCH ₃	28		
OCH ₃	OCH ₃		370	354

The validity of the above relationship was examined in terms of wave number, reciprocal of wavelength, and it was found that the following relationship is also hold in good agreement.

$$\bar{\nu} = \bar{\nu}_0 - (\Delta\bar{\nu}_x + \Delta\bar{\nu}_y) \quad (2)$$

where $\bar{\nu}$ and $\bar{\nu}_0$ are the wave number of di- and non-substituted azoxybenzenes respectively, and $\Delta\bar{\nu}_x$ is the difference of wave number between 4-x-substituted azoxybenzene and azoxybenzene; $\Delta\bar{\nu}_y$ is that for 4-y-substituted azoxybenzene and azoxybenzene. The agreements are shown in Table III.

TABLE III

The comparison of the observed $\bar{\nu}$ and calculated $\bar{\nu}$ of the $\pi \rightarrow \pi^*$ transition band of azoxybenzenes

X	Y	$\Delta\bar{\nu}_x \times 1000$	$\Delta\bar{\nu}_y \times 100$	$\bar{\nu} \times 1000$ calcd.	$\bar{\nu} \times 1000$ obsd.
CH ₃	H	0.0381			
H	CH ₃		6.0752		
CH ₃	CH ₃			2.99	2.99
Br	H	0.0568			
H	Br		0.0660		
Br	Br			2.98	2.98
CH ₃	H	0.0381			
H	Br		0.0660		
CH ₃	Br			3.00	2.99
Br	H	0.0568			
H	CH ₃		0.0752		
Br	CH ₃			2.97	2.98
OCH ₃	H	0.182			
H	CH ₃		0.0752		
OCH ₃	CH ₃			2.85	2.86
OCH ₃	H	0.182			
H	OCH ₃		0.248		
OCH ₃	OCH ₃			2.68	2.82

Since the product of wave number and hc is equal to energy, $\epsilon = hc\bar{\nu}$, which is the amount of energy to promote the π electron to the excited state, π^* , the equation (2) stipulates that the $\pi \rightarrow \pi^*$ transition could be aided by the introduction of the substituents in *para*-positions by the factor of $\Delta\bar{\nu}_x$ and $\Delta\bar{\nu}_y$.

Then we can see easily that the $\Delta\bar{\nu}_x$ and $\Delta\bar{\nu}_y$ are the factor of inductive and resonance contribution of the substituents for the narrowing effect of $\pi \rightarrow \pi^*$ transition energy level in the spectra of disubstituted azoxybenzenes. The applicability of this relationship for *meta* and *ortho* substituted azoxybenzenes, and for some other compound(s) needs further investigation.

Experimental

The preparation of the compounds used in this study was described in the previous paper.⁹ The symmetrical disubstituted azoxybenzenes were synthesized by the same method using 4-substituted nitrosobenzenes.

cis-Azoxybenzene was prepared as follows. Fifteen grams of nitrosobenzene in 300 ml. of 95% EtOH was added immediately to a mixture of 30 ml. of 2N-NaOH and 40 ml. of 95% EtOH keeping temperature below 9°C. After the addition, the temperature was raised at 23°C. for 90 minutes, and then brown precipitate formed. Neutralized with ca. 1N HCl and poured into water, from which the precipitate was obtained for a long standing at room temperature. The precipitate was triturated with cold ligroin and recrystallized 3 times from cold MeOH. White leaf-like crystals, M.P. 84°C (Lit.¹⁰ M.P. 84°C).

The spectra were measured by using a Beckman Model DU quartz spectrophotometer and a Cary Model 11 recording spectrophotometer.

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