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Substituents Effects on the Azo-Hydrazone Tautomerism of 4-Arylazo-2,6-di-*t*-butylphenols

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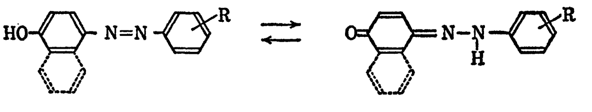
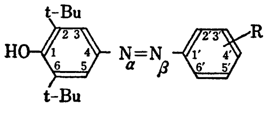
The substituents effects on the azo-hydrazone tautomerism of 4-arylazo-2,6-di-*t*-butylphenols in carbon tetrachloride were studied by means of infrared and visible spectra. The substituents effects on their absorption spectra were discussed. The azo tautomers are predominant in the tautomeric equilibria of 3'- and 4'-substituted derivatives. Considerable participations of the hydrazone tautomers are found in the equilibria of the 2'-substituted derivatives having substituents capable of forming intramolecular hydrogen bonding with hydrazone-hydrogen atom. In the equilibria of 2',6'-disubstituted derivatives, the positions of the equilibria move somewhat to the azo side from those of the corresponding 2'-substituted derivatives.

It is well known that the hydroxyazo dyes (I) show the azo-hydrazone tautomerism:



(I) - azo tautomer (I) - hydrazone tautomer

Many papers have been given on the naphthol derivatives of the dyes (I) since their tautomeric equilibria were found to show remarkable changes with their substituents and the solvents.[1–10] It has been observed that the electron-releasing substituents and the non-polar solvents favor the azo tautomers in equilibria. There are few papers on the phenol derivatives of (I). This might be due to the fact that the azo tautomers have been found predominant in equilibria. 4-Arylazo-2,6-di-*t*-butylphenols (II), which are the derivatives of hydroxyazo dyes (I), were prepared. The infrared and visible spectra of the phenols (II) in carbon tetrachloride solution showed interesting substituent effects on the tautomerism.



(II)

Results and Discussion

The results are summarised in Table 1.

Infrared Spectra. It has been pointed out that the dyes (I) show significant differences in their infrared spectra and that, among many absorption bands, the characteristic bands are the ν_{OH} band of the azo tautomer and the ν_{NH} and ν_{CO} bands of the hydrazone tautomer.[5,6] In this paper, each tautomer was studied by means of the ν_{OH} and the ν_{NH} bands, respectively, since the ν_{CO} bands appeared in the absorption region of the solvent.

ν_{OH} *Bands*: It has been reported that the ν_{OH} bands of (I) were sometimes found in the region of the ν_{NH} bands as a result of the hydrogen bondings, and some difficulties were encountered to distinguish the respective bands.[5] The infrared spectra of the azo tautomers of the phenols (II) always show sharp, monomeric ν_{OH} bands.[11] The bands are located nearly always at *ca.* 3640 cm^{-1}, while ν_{OH} bands of 4-substituted-2,6-di-*t*-butylphenols have been reported to shift within the region 3649—3626 cm^{-1} with their substituents.[12] The intensities vary with the substituents and tend to become smaller when the substituents displace the positions of the equilibria towards the hydrazone side.

ν_{NH} *Bands*: The bands are found in the region 3380—3280 cm^{-1} and the locations and the intensities vary not only with the substituents but also with substituting positions. Of 3'- and 4'-substituted derivatives, 4'-nitro derivative has a trace of ν_{NH} band, but no other derivative has it. Of 2'-substituted derivatives, methoxy, halogen and nitro derivatives have ν_{NH} bands, but not methyl derivative. The bands are due to the hydrazone tautomers which are favored in the equilibria by the additional stabilisation of the intramolecular hydrogen bonding between 2'-substituent and hydrazone-hydrogen atom.[6] The bands are also found in the spectra of 2',6'-dichloro, 2',6'-dibromo, 2',6'-dinitro, 2',4'-dinitro, and 2',4',6'-trinitro derivatives, in which intramolecular hydrogen bondings are also possible. The wave numbers of the ν_{NH} bands give the following order of locations:

$$2',4',6'\text{-}(\mathrm{NO_2})_3 — 2',6'\text{-}(\mathrm{NO_2})_2 — 2',4'\text{-}(\mathrm{NO_2})_2 — 2'\text{-}\mathrm{NO_2}$$
$$— 2',6'\text{-}\mathrm{Cl_2} — 2',6'\text{-}\mathrm{Br_2} — 2'\text{-}\mathrm{Br_2} — 2'\text{-}\mathrm{Cl} — 2'\text{-}\mathrm{MeO} — 2'\text{-}\mathrm{F}$$

The order might not be the order of the strengths of the intramolecular hydrogen bondings since the locations of the ν_{NH} bands have been observed to shift towards lower wave numbers with electron-attracting substituents in the unassociated 4-arylazo-1-naphthols

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Table 1. Spectral data of the phenols (II)

	Infrared spectra		Visible spectra				
R of II	ν_{OH} band cm^{-1}	ν_{NH} band cm^{-1}	Azo band λ_{max} mμ	ε_a	Hydrazone band λ_{max} mμ	ε_a	$\frac{\varepsilon_a}{\varepsilon_a+\varepsilon_h}$
2′-MeO	3643 w	3372 m	365	6.42×10^3	454	2.67×10^4	0.19
3′-MeO	3641 s	—	358	2.40×10^4	442	2.55×10^3	0.90
4′-MeO	3641 s	—	359	2.41×10^4	447	2.51×10^3	0.91
2′-Me	3643 s	—	357	2.24×10^4	450	2.22×10^3	0.91
3′-Me	3644 s	—	353	2.12×10^4	442	2.97×10^3	0.88
4′-Me	3644 s	—	354	2.27×10^4	443	1.48×10^3	0.94
Unsubstituted	3641 s	—	352	2.51×10^4	443	2.40×10^3	0.91
2′-F	3642 s	3381 vw	359	1.98×10^4	433	8.22×10^3	0.71
4′-F	3644 s	—	353	2.45×10^4	440	2.10×10^3	0.92
2′-Cl	3639 m	3365 w	370	1.15×10^4	434	1.71×10^4	0.62
3′-Cl	3639 s	—	358	2.27×10^4	437	2.84×10^3	0.89
4′-Cl	3645 s	—	360	2.93×10^4	438	2.17×10^3	0.93
2′-Br	3644 m	3358 w	368	1.47×10^4	434	1.81×10^4	0.55
4′-Br	3639 s	—	361	2.90×10^4	441	2.28×10^3	0.93
4′-COOEt	3641 s	—	369	2.61×10^4	438	7.83×10^3	0.77
2′-NO_2	—	3314 m	396	1.77×10^4	458	2.70×10^4	0.40
3′-NO_2	3639 s	—	366	1.86×10^4	434	2.22×10^3	0.89
4′-NO_2	3641 s	3363 trace	388	2.33×10^4	440	1.11×10^4	0.68
2′,6′-Me_2	3642 s	—	336	2.10×10^4	442	1.59×10^3	0.93
2′,6′-F_2	3640 s	—	348	1.97×10^4	426	2.40×10^3	0.89
2′,6′-Cl_2	3639 s	3356 w	340	1.31×10^4	408	8.90×10^3	0.60
2′,6′-Br_2	3639 s	3340 trace	341	1.75×10^4	422	2.34×10^3	0.88
2′,6′-$(NO_2)_2$	3638 trace	3300 w	392	2.21×10^4	437	1.97×10^4	0.53
2′,4′-$(NO_2)_2$	—	3308 m	399	3.04×10^4	438	3.51×10^4	0.46
2′,4′-6′-$(NO_2)_3$	—	3283 m	—		410	3.97×10^4	0

vw, w, m, s; relative intensities

ε_a, ε_h; molar extinction coefficients of azo and hydrazone bands, respectively.

in which the intramolecular hydrogen bondings are impossible.[6] Besides, the hydrogen bondings in 2′,6′-disubstitted derivatives can be disturbed by the twisting of aryl nuclei. The molecular model inspections for the hydrazone tautomers of such geometries that the quinone nuclei and the aryl nuclei are in the same plane show that the distance between α-nitrogen atom and 2′-chlorine atom is *ca.* 2.3 Å, and the distance between α-nitrogen atom and the oxygen atom of 2′-nitro group is *ca.* 1.4 Å. Thus, it is very likely that aryl nuclei are twisted as a result of large steric repulsions.

Visible Spectra. The phenols (II) have two absorption maxima in the region 340—460 mμ and substituents change their locations and the molar extinction coefficients (ε) of the absorption maxima. It is well known that the hydroxyazo dyes (I) have two absorption maxima in the region 320—480 mμ, and the absorptions at shorter wavelengths originate from azo tautomers and the absorptions at longer wavelengths from hydrazone tautomers.[1–10,13,14] It is concluded from a comparison between infrared and visible spectra that the phenols (II) follow this relation. This is also supported by the fact that untautomerising 2,6-di-*t*-butyl-*p*-benzoquinone-*N*-methylphenylhydrazone has its absorption maximum at 437 mμ.

Azo Bands: Figure 1 gives the correlation of the Hammett substitution constants[15] and the wavelengths of the absorption maxima of the azo bands of 3′- and 4′-substituted derivatives. It is observed that the substituents of larger electron-releasing or -attracting powers show larger bathochromic effects, in which an anomalously large shift is caused by 4′-nitro group, and the shift by 3′-substituents are smaller than those by 4′-substituents. The absorptions may be due to π–π* transitions of the completely conjugated π-electron systems of azo tautomers.[16] 2′-Substituted derivatives show bathochromic shifts to 3′- and 4′-isomers although hypsochromic shifts are expected because of the steric interaction between 2′-substituents and azo group. Thus, the observed bathochromic shifts might be due to the electronic effects of 2′-substituents stronger than 3′- and 4′-substituents. 2′, 6′-Disubstituted derivatives, except for dinitro derivative, have their absorption maxima at wavelengths shorter than the corresponding 3′- and 4′-substituted derivatives. The planer conformations of 2′,6′-disubstituted derivatives are impossible because of the steric repulsion between azo group and substituents. The molecular model inspection for the co-planer azo tautomer of 2′,6′-dichloro derivative show that the distance between α-nitrogen atom and 2′-

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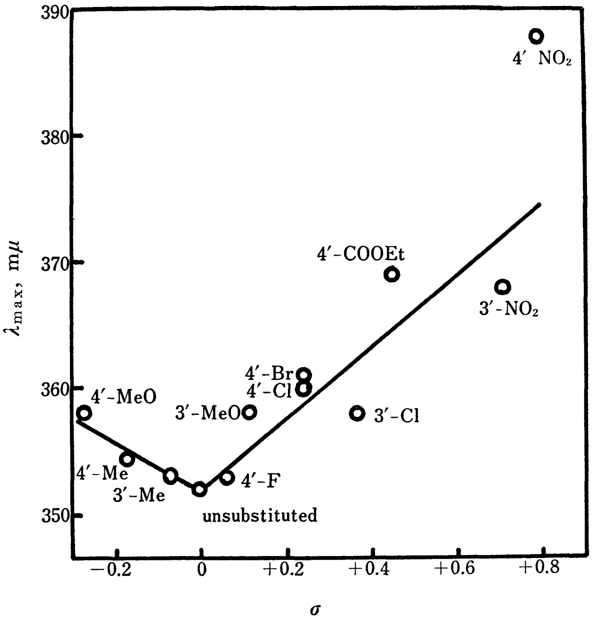

Fig. 1. The correlation of the Hammett substitution constants with the wavelength of the azo bands of 3'- and 4'-substituted phenols (II).

chlorine atom is *ca.* 2.5 Å and that between β-nitrogen atom and 6'-chlorine atom is *ca.* 2.9 Å. Thus, the twist of the aryl nuclei may exist in the actual molecules and give rise to hypsochromic shifts. The bathochromic shift of 2',6'-dinitro derivative may be due to the overwhelming electronic effects of two nitro groups.

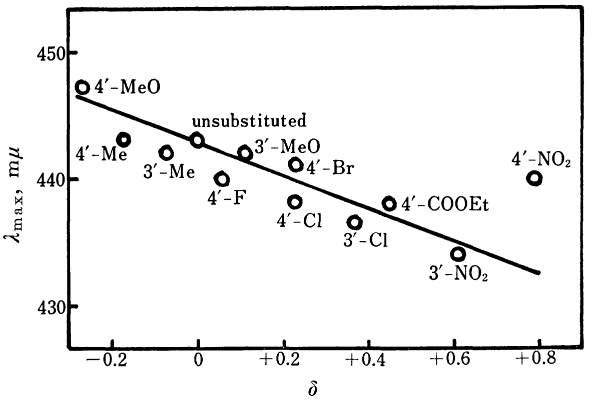

Fig. 2. The correlation of the Hammett substitution constants with the wavelength of the hydrazone bands of 3'- and 4'-substituted phenols(II).

Hydrazone Bands: Figure 2 gives the correlation of the Hammett substitution constants and the wavelengths of the absorption maxima of the hydrazone bands of 3'- and 4'-substituted derivatives. The electron-releasing substituents have the trend to shift the absorption maxima towards longer wavelengths and the electron-attracting substituents have the opposite trend. The same trend is observed in 2'-substituted derivatives except for 2'-nitro derivative. The bathochromic shift in 2'-nitro derivative is due to the strong intramolecular hydrogen bonding. 2',6'-Disubstituted derivatives have the same trend as in 3'- and 4'-derivatives. But the locations of the absorption maxima are displaced to wavelengths shorter than those of the corresponding 2'-substituted derivatives owing to the twist of the aryl nuclei.

Tautomeric Equilibria. The position of the tautomeric equilibrium can be estimated with molar extinction coefficients ε at the absorption peaks in the infrared or visible spectra. The visible spectra, however, show that the disappearance of the ν_{NH} bands in the infrared spectra does not mean the absence of hydrazone tautomers. The small amount of the hydrazone tautomer will erase the weak ν_{NH} band. The position of the equilibria should be discussed by means of the molar extinction coefficients in the visible spectra when the true molar extinction coefficients of the individual tautomers are known and the location of the absorption maxima are separated sufficiently from each other.[3] On account of the above restrictions, the tautomeric equilibria of the phenols (II) can not be discussed quantitatively. The values of the ratio $\varepsilon_{\text{azo band}}/\varepsilon_{\text{azo band}} + \varepsilon_{\text{hydrazone band}}$ are caluculated in Table 1 since the values should indicate the positions of the tautomeric equilibria indirectly. The conclusions from these values and the infrared spectra are as follows. The azo tautomers are predominant in the tautomeric equilibria of 3'- and 4'-substituted derivatives. The electron-releasing substituents favor the hydrazone tautomers in equilibria. Considerable participation of the hydrazone tautomers is found in the equilibria of 2'-substituted derivatives having substituents which can form the intramolecular hydrogen bondings with the hydrazone-hydrogen atoms since the hydrazone tautomers are stabilised by intramolecular hydrogen bonding. In the equilibria of 2',6'-disubstituted derivatives, the positions of the equilibria move somewhat to the azo side from those of the corresponding 2'-substituted derivatives. The disubstitution at 2'- and 6'-positions may disturb the intramolecular hydrogen bonding and diminish the stabilisation for hydrazone tautomers. In the equilibrium of 2',4',6'-trinitro derivative, however, the electronic effect is so large that the hydrazone tautomer is completely predominant.

Experimental

Phenols (II) were prepared through the condensation of 2,6-di-*t*-butyl-*p*-benzoquinone with arylhydrazine hydrochlorides or arylhydrazines (in case of dinitro and trinitro derivatives). Preparation of 4'-methyl derivative gives a typical example as follows: 2,6-di-*t*-butyl-*p*-benzoquinone (1.67 g, 0.0076 mol) was added to the ethanol solution (100 m*l*) of *p*-tolylhydrazine hydrochloride (1.45 g, 0.0091 mol), containing concentrated hydrochloric acid (5 m*l*). After the reaction mixture was kept standing for one week at room temperature, yellow crystals of 4-(4'-tolylazo)-2,6-di-*t*-butylphenol were precipitated by careful addition of water (*ca.* 30 m*l*) to the reaction mixture. The prepared phenols (II) were purified with recrystalisations from ethanol and silica gel column chromatography. The following melting points (°C) were observed for each crystal; 2'-MeO: orange plates, 163.4—164.0. 3'-MeO: yellow needles, 126.6—128.6.

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4′-MeO: yellow plates, 114.0—114.5. 2′-Me: orange powder, 113.5—119.5. 3′-Me: orange powder, 88.5—92.5. 4′-Me: yellowish orange needles, 135. —136.0. Unsubstituted: red needles, 98.0—99.0. 2′-F: yellowish orange needles, 101.6—103.6. 4′-F: yellowish orange needles, 106.0—107.0. 2′-Cl: reddish orange plates, 134.4—135.4. 3′-Cl: orange needles, 102.8—103.8. 4′-Cl: orange needles. 138.0—139.0. 2′-Br: orange plates, 154.0—155.5. 4′-Br: orange needles, 151.8—152.8. 4′-COOEt: yellow needles, 186.4—187.4. 2′-NO_2: red plates, 158.5—159.5. 3′-NO_2: yellowish orange needles, 162.5—163.5. 4′-NO_2: red plates, 191.0—192.5. 2′,6′-Me_2: reddish orange needles, 117.5—118.5. 2′,6′-F_2: orange plates, 123.8—125.8. 2′,6′-Cl_2: yellowish orange plates, 110.8—111.5. 2′,6′-Br_2: orange needles, 123.5—125.0. 2′,6′-$(NO_2)_2$: red needles, 156.0—157.0. 2′,4′-$(NO_2)_2$: yellow needles, 185.5—188.0. 2′,4′,6′-$(NO_2)_3$: violet plates, 202.0—203.0. 2′,6′-Di-*t*-butyl-*p*-benzoquinone-*N*-methylphenylhydrazone (red needles, mp 127.0—127.5°C) was prepared from 2,6-di-*t*-butyl-*p*-benzoquinone and α-methyl-α-phenylhydrazine by the same method. Results of elementary analyses for the prepared compounds were in good agreement with theoritical values. The infrared spectra of the phenols (II) in carbon tetrachloride solution of 4.00×10^{-3} M in 1 mm NaCl cell were recorded with Shimadzu IR-27G Grating Spectrophotometer. The visible spectra of the phenols (II) in carbon tetrachloride solution of 2.00×10^{-3} M in 0.11 mm quartz cell were recorded with Hitachi EPS-2U Recording Spectrophotometer. BeOr's law was valid for the concentration higher than 5.00×10^{-3} M.