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Effects of Substituents on pK_a and τ_{OH} Values of Hydroxyaryl-1,3,5-triazines; σ_p^- Values of 1,3,5-Triazinyl Groups.

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Synopsis. Regular relations were found between substituents in the *s*-triazine nucleus and pK_a values, τ_{OH} values of *o*- and *p*-hydroxyphenyl-*s*-triazines, and stabilities of chelation of the *o*-isomers. The substituent constants (σ_p-) for some *s*-triazinyl groups were also found.

No detailed information has been given on the relation between chemical constitutions of 2-(*o*-hydroxyaryl)-nitrogen heteroaromatics and their stability of chelation because of the difficulty of obtaining a series of 2-(*o*-hydroxyaryl)-nitrogen heteroaromatics. However, a number of hydroxyaryl-*s*-triazines are readily available by the photolysis of aryloxy-chloro-*s*-triazines followed by treatment with nucleophiles.[1] These *s*-triazine derivatives can provide an appropriate series of 2-(*o*-hydroxyaryl)-nitrogen heteroaromatic for studying the substituent effects on the strength of chelation. This paper deals with the effects of substituents in the *s*-triazine nucleus on pK_a value and ^1H chemical shift of phenolic proton of hydroxyaryl-*s*-triazine giving substituent constants for the *s*-triazine nucleus.

Experimental

The NMR spectra were recorded on a Varian A-60D spectrometer in DMSO-d_6 with tetramethylsilane as an internal standard, and the pK_a values were measured spectrophotometrically in water at 25 °C.

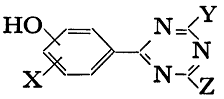
Materials. Hydroxyaryl-*s*-triazines were synthesized by the method described previously.[1]

Results and Discussion

pK_a Values of Hydroxyaryl-s-triazines. In the ordinary chelated phenols the stabilities of chelation are regularly correlated with their pK_a values. Thus, the stabilities of chelation of *o*-hydroxyaryl-*s*-triazines were discussed in connection with their pK_a values. The pK_a values of various hydroxyaryl-*s*-triazines are given in Table 1.

We see that the pK_a values of *o*-hydroxyphenyl-*s*-triazines are higher than those of the corresponding *p*-isomers, suggesting that chelate ring formation takes place in each *o*-hydroxyphenyl-*s*-triazine. The pK_a values of *o*- and *p*-hydroxyphenyl-*s*-triazines vary regularly with two substituents in the *s*-triazine nucleus [$pK_a(o) = -0.890\ \sum\sigma_m + 11.37$, where $\sum\sigma_m$ denotes a summation of σ_m values of two substituents in the *s*-triazine nucleus]. However, the pK_a values of *p*-hydroxyphenyl-*s*-triazines were affected to a lesser extent than the *o*-isomers by the substituents in the *s*-triazine nucleus; the relatively large difference in pK_a value between the *o*-hydroxyaryl-*s*-triazines is considered

TABLE 1. pK_a VALUES AND ^1H CHEMICAL SHIFTS OF PHENOLIC PROTONS OF HYDROXYARYL-*s*-TRIAZINES



No.	HO–	X	Y	Z	pK_a	τ_{OH}
1	*o*-OH	H	$-OC_6H_5$	$-OC_6H_5$	10.92	−1.57
2	*o*-OH	H	$-OC_6H_5$	$-OCH_3$	11.06	−1.93
3	*o*-OH	H	$-OCH_3$	$-OCH_3$	11.17[a)]	−2.52[a)]
4	*o*-OH	H	$-OC_6H_5$	$-N(CH_3)_2$	11.29	−2.57
5	*o*-OH	H	$-N(CH_3)_2$	$-N(CH_3)_2$	11.76	−3.75
6	2-OH	5-CH_3	$-OC_6H_4-CH_3$(*p*)	$-OC_6H_4-CH_3$(*p*)	11.45	−1.37
7	2-OH	5-CH_3	$-OC_6H_4-CH_3$(*p*)	$-OCH_3$	11.61	−1.77
8	2-OH	5-CH_3	$-OCH_3$	$-OCH_3$	11.71[a)]	−2.31[a)]
9	2-OH	5-CH_3	$-OCH_3$	$-N(CH_3)_2$	11.94	−2.92
10	2-OH	5-CH_3	$-N(CH_3)_2$	$-N(CH_3)_2$	12.23	−3.13
11	*p*-OH	H	$-OC_6H_5$	$-OC_6H_5$	—	−0.35
12	*p*-OH	H	$-OC_6H_5$	$-OCH_3$	8.37	−0.27
13	*p*-OH	H	$-OCH_3$	$-OCH_3$	8.46[a)]	−0.18[a)]
14	*p*-OH	H	$-OC_6H_5$	$-N(CH_3)_2$	8.55	−0.10
15	*p*-OH	H	$-OCH_3$	$-N(CH_3)_2$	8.65	−0.07
16	*p*-OH	H	$-N(CH_3)_2$	$-N(CH_3)_2$	8.88	+0.12
17	2-OH	5-Cl	$-OCH_3$	$-OCH_3$	10.39[a)]	−2.64[a)]
18	2-OH	6-H	$-OCH_3$	$-OCH_3$	11.17[a)]	−2.52[a)]
19	2-OH	6-OCH_3	$-OCH_3$	$-OCH_3$	11.97[a)]	−2.10[a)]

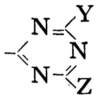
a) reported in the previous paper.[1]

to be due not only to the difference in the original acidity of *s*-triazinyl-phenol but also to the difference in stability of the chelation. If steric requirements in all the *o*-hydroxyaryl-*s*-triazines are similar in magnitude as might be anticipated in these cases, the relative strength of intramolecular hydrogen bond can be evaluated by means of the difference in pK_a value between *o*- and corresponding *p*-hydroxyaryl-*s*-triazines [ΔpK_a=p$K_a(o)-$p$K_a(p)$]. When ΔpK_a values are plotted against the $\sum\sigma_m$ values, a straight line of negative slope (Δp$K_a=-0.248\ \sum\sigma_m+2.77$) was obtained, suggesting that the stability of chelation varies with the substituents in the *s*-triazine nucleus, although the substituent effect is small. Similar relations were also observed in the case of 5-methyl-2-hydroxyphenyl-*s*-triazines, showing that the greater the electron-donating tendency of the two substituents in the *s*-triazine nucleus, the higher the pK_a value owing to the formation of stronger chelated ring due to an increase in electron density at the ring nitrogen atom. Thus, among the *o*-hydroxyaryl-*s*-triazines of the same phenol moiety the relative stability of chelation can be represented by the summation of σ_m values of two substituents in the *s*-triazine ring.

*Chemical Shifts of Hydroxyl Protons of Hydroxyaryl-*s*-triazines.* Substituent effects on the chemical shifts of hydroxyl protons of hydroxyaryl-*s*-triazines were investigated. Effects of substituents on the NMR signals of phenolic protons have been studied with many substituted phenols;[2] in each case a good correlation holds between the substituents in the *meta* and *para* positions and ^{1}H chemical shifts of phenolic protons. ^{1}H Chemical shifts (in τ) of phenolic protons of hydroxyaryl-*s*-triazines are given in Table 1. In this case also the difference in τ_{OH} value between *p*-*s*-triazinylphenols is relatively small [$\tau_{OH}(p)=-0.487\ \sum\sigma_m-0.091$]; the large difference in τ_{OH} value between *o*-isomers [$\tau_{OH}(o)=2.27\ \sum\sigma_m-2.79$] being ascribed to the difference in the strength of chelation. A linear relation holds between the $\Delta\tau_{OH}[\Delta\tau_{OH}=\tau_{OH}(o)-\tau_{OH}(p)]$ and $\sum\sigma_m$ values ($\Delta\tau_{OH}=-2.77\ \sum\sigma_m+2.71$). Similar relations are also observed in the case of 5-methyl-2-hydroxyphenyl-*s*-triazines. Thus, among the *o*-hydroxyaryl-*s*-triazines of the same phenol and different *s*-triazine moieties, not only the ΔpK_a and $\Delta\tau_{OH}$ values but also the $\sum\sigma_m$ values of two substituents in the *s*-triazine nucleus can be utilized as a measure for the relative stability of chelation.

Substituent Constants of s-*Triazinyl Groups.* The *s*-triazinyl group is known as an electron-attracting substituent. However, so far there has been no quantitative evaluation for the electron-withdrawing powers of common *s*-triazinyl groups. In the *p*-hydroxyphenyl-*s*-triazines, each pK_a value was smaller than that of phenol, indicating that the *s*-triazinyl group is electron-attracting regardless of two substituents in the *s*-triazine nucleus. However, the pK_a value of this series also varies regularly with the $\sum\sigma_m$ value [p$K_a(p)=-0.635\ \sum\sigma_m+8.60$].

Table 2. σ_p^- values of *s*-triazinyl groups



Y	Z	$\sum\sigma_m$ (σ_mY+σ_mZ)	σ_p^- (a)	σ_p^- (b)	σ_p^- (d)
–Cl	–Cl	0.747	(0.82)[c)]	(0.88)[c)]	0.85
$-OC_6H_5$	$-OC_6H_5$	0.504	—	0.80	0.80
$-OC_6H_5$	$-OCH_3$	0.367	0.71	0.75	0.73
$-OCH_3$	$-OCH_3$	0.230	0.66	0.70	0.68
$-OC_6H_5$	$-N(CH_3)_2$	0.041	0.61	0.63	0.62
–H	–H	0	(0.60)[c)]	(0.62)[c)]	0.61
$-OCH_3$	$-N(CH_3)_2$	−0.096	0.57	0.59	0.59
$-N(CH_3)_2$	$-N(CH_3)_2$	−0.422	0.47	0.47	0.47

a) obtained from pK_a values using the Hammett equation of Biggs and Robinson.[3] (pK_a=9.92—2.23σ_p^-). b) obtained from τ_{OH} values using the Hammett equation of Quellette[2] (τ_{OH}=0.774—1.40σ_p^-). This equation was obtained using the results of Quellette by the method of least squares. c) obtained using correlation equations between σ_p^- and $\sum\sigma_m$ values; in the case of (a) series, $\sigma_p^-=0.30\sum\sigma_m+0.60$; in the case of (b) series, $\sigma_p^-=0.35\sum\sigma_m+0.62$. d) mean value of σ_p^-.

Since a good linear relation holds between the substituent and dissociation constants of phenols (p$K_a=-2.23\sigma+9.92$),[3] substituent constants for the *s*-triazinyl groups of σ_p^- character can be obtained from the pK_a values of *p*-*s*-triazinylphenols. The results are given in Table 2. When these σ_p^- values are plotted against the $\sum\sigma_m$ values, a straight line with a positive slope of 0.30 is obtained, indicating that the substituents in the *s*-triazine nucleus affect the electron-attracting power of *s*-triazine nucleus only to a minor extent.

In the case of τ_{OH} value, a linear correlation is also observed between the $\sum\sigma_m$ and τ_{OH} values of *p*-hydroxyphenyl-*s*-triazines. Substituent constants attributable to *s*-triazinyl groups were also obtained from τ_{OH} values using an equation obtained by plotting τ_{OH} values of substituted phenols[2] against the substituent constants σ_p^-.

The σ_p^- values of the two series agree fairly well. $\sum\sigma_m$ was found to become zero at $\sigma_p^-=0.61$, indicating the *s*-triazinyl group itself to be a fairly electron-attracting substituent. The bis(dimethylamino)- and dichloro-*s*-triazinyl groups were found to have the smallest and greatest σ_p^- values of the common *s*-triazinyl groups, being 0.47 and 0.85, respectively. This shows that the electron-attracting powers of the common *s*-triazinyl groups are comparable to those of ordinary acyl and other related groups.

References

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3) A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, **1961**, 388.