Substituent Effect on the Dissociation Constants of 5-(Substituted Styryl)-2-aminotropones

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The dissociation constants of various 5-styryl-2-aminotropones were determined spectrophotometrically using 50%(v/v) aqueous methanol and correlated by the use of Hammett equation, with $\rho=0.57$.

The quantitative estimation of the transmission of electronic effects through a system of conjugated double bonds is of great theoretical importance and has attracted the attention of many chemists. The most convenient systems are aromatic compounds of the R–C_6H_4–CH=CH–G–Y type, where G is an aromatic ring, such as benzene, pyridine, and tropone. The dissociation constants of various 4-aminostilbenes (G=C_6H_4, Y=NH_2),[1] 4-hydroxystilbenes (G=C_6H_4, Y=OH),[2] and 4-styrylpyridines (G=C_5H_4N)[3] and the chemical shifts of 4-fluorostilbenes (G=C_6H_4, Y=F)[4] have been measured in the past. It has been found that the electronic effect of the substituent in one ring is transmitted through the ethylene linkage to the reaction center in another ring and correlated by the Hammett equation.

Previously, we reported the substituent effects on the dissociation constants of 4-[5] and 5-styryltropolones[6] and 4- and 6-styryl-2-aminotropones.[7] However, the substituent effect in 5-styryl-2-aminotropones has not been investigated. In the present study, the dissociation constants of several 5-styryl-2-aminotropones, shown in Fig. 1, were measured spectrophotometrically, and the electronic effects of the substituents on their dissociation constants were discussed quantitatively.

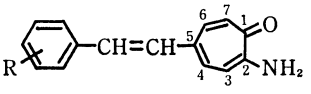

Fig. 1.

Results and Discussion

The dissociation constants of 5-(*p*-methoxystyryl)-, 5-(*p*-methylstyryl)-, 5-(*m*-methylstyryl)-, 5-styryl-, 5-(*m*-methoxystyryl)-, and 5-(*p*-chlorostyryl)-2-aminotropones were determined spectrophotometrically in 50%(v/v) aqueous methanol at 23 °C. Their pK_a values are listed in Table 1, together with their mp's. The pK_a value (2.21) of 5-styryl-2-aminotropone is smaller than those of 4- and 6-styryl-2-aminotropones (pK_a 2.54 for 4-styryl and 2.57 for 6-styryl isomers).[7] This might be mainly due to the conjugate interaction between the amino group and the styryl group in 5-styryl-2-aminotropones. Further, 5-styryl-2-aminotropones show pK_a values between 2.05 (*p*-chloro) and 2.35 (*p*-methoxy) and are less basic than *p*-(substituted styryl)anilines (*i.e.*, 3'- and 4'-substituted 4-aminostilbenes [pK_a 3.67 (*p*-chloro) to 3.86 (*p*-methoxy)]).[1] This may be attributed to the electron-withdrawing effect of the carbonyl group adjacent to the amino group in the tropone nucleus.

TABLE 1. pK_a VALUES OF 2-AMINO-5-STYRYLTROPONES IN 50%(v/v) METHANOL

No.[a]	R	Mp (°C)	$c\times10^5$ (mol/l)	λ (nm)	pK_a
1	*p*-OCH_3	244—245	1.640	290	2.35±0.05
2	*p*-CH_3	232—234	1.881	284	2.28±0.03
3	*m*-CH_3	172	1.991	282	2.24±0.04
4	H	205—206[b]	2.273	280	2.21±0.07
5	*m*-OCH_3	162	1.877	287	2.15±0.05
6	*p*-Cl	231—232	1.585	283	2.05±0.03

a) Numbers correspond to those given in Fig. 2.
b) Mp 205—206 °C (Ref. H. Matsumura, *Nippon Kagaku Zasshi*, **81**, 1763 (1960)).

When the pK_a values of 5-styryl-2-aminotropones are plotted against the Hammett substituent constants, σ,[8] of the substituent in the benzene ring, the plot gives the straight line shown in Fig. 2, and the following equation is obtained by the least-squares method:

$$pK_a = 2.20 - 0.57\,\sigma \quad (r=0.991)$$

In the case of 4- and 6-styryl-2-aminotropones, the effects of the substituents in the benzene ring are mainly transmitted to the amino group in the tropone nucleus by the inductive effect, while the styryl group in 5-styryl-2-aminotropones is located at a position where resonance interaction between the styryl group and the reaction center of tropone nucleus is possible; therefore, the transmission of the electronic effects by the fairly large resonance effect as well as by the inductive effect can be expected. The ρ values of 4-, 5-, and 6-styryl-2-aminotropones are listed in Table 2. When the 4-styryl and 6-styryl derivatives are compared

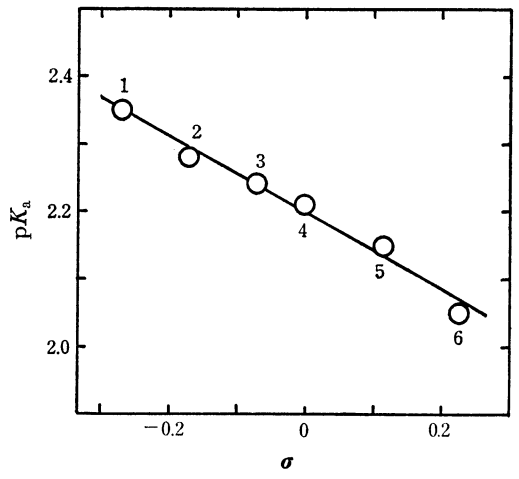

Fig. 2. The Hammett plot of pK_a's of 2-amino-5-styryltropones.

TABLE 2. THE ρ VALUES OF 4-, 5-, AND 6-STYRYL-2-AMINOTROPONES

Styryl-substituted 2-aminotropones	ρ
4-Styryl	0.59
5-Styryl	0.57
6-Styryl	0.40

with each other, the ρ value of the 4-styryl isomers is larger than that of the 6-styryl isomers because of the difference in distance between the styryl group and the amino group. On the other hand, the distance of the 5-styryl group in this work from the amino group is almost equal to that in the case of the 6-styryl derivatives. In other words, it may be assumed that the transmissibility which is caused by the inductive effect is almost equal in the 5- and 6-styryl derivatives. Thus, it is thought that a part of the ρ value of the 5-styryl isomers is due to the resonance effect mentioned above and is comparable to the difference in the ρ values based on the inductive effect, which is caused by the difference in distance from the 4- and 5-styryl groups to the amino group. Our results revealed that transmission through the styryl group varies with the position at which the styryl group is attached, the values being reduced in this order:

$$\text{4-styryl} \simeq \text{5-styryl} > \text{6-styryl}$$

Next, the dissociation constants were determined in 50%(v/v) aqueous ethanol at 25 °C. The Hammett analysis of them gave the following linear regression:

$$pK_a = 2.02 - 0.92\,\sigma \quad (r=0.992)$$

This ρ value is larger than that in 50% aqueous methanol. Such a difference is also observed[8] in the dissociation of benzoic acids, the ρ values being 1.085 in 50% aqueous methanol and 1.601 in 50% aqueous ethanol. It is thought that the difference between the two media is attributable to their polarity. Furthermore, the ρ value of 5-styryl-2-aminotropones is larger than the value for the dissociation of 4-aminostilbenes (0.42 in 50% aqueous ethanol at 20 °C).[1] This might be due to the fact that the tropone nucleus is charged slightly by the polarization of the carbonyl group. It is thought that there is some conjugate interaction between the styryl group and the carbonyl group.

Experimental

Materials. The 5-(substituted styryl)-2-aminotropones were prepared by the abnormal substitution reaction of 2-chloro-4-styryltropones, which has themselves been obtained from 4-styryltropolones in three steps. This method will be described elsewhere. Their melting points are listed in Table 1.

Measurement of Dissociation Constants. The dissociation constants of the 2-amino-5-styryltropones were measured spectrophotometrically in 50% aqueous methanol at 23 °C and in 50% aqueous ethanol at 25 °C, using the method of Albert and Serjeant.[9] The constants were obtained by using this equation:

$$pK_a = pH + \log \frac{A_B - A}{A - A_{BH^+}}$$

where A_B and A_{BH^+} are the absorbance of the base and its conjugate acid respectively. The absorption spectra were taken on a Hitachi EPS-3T spectrophotometer, while the pH values were measured by mean of Hitachi-Horiba F-7 pH meter.

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