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Dissociation Constants of 2-Aminotropones

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Synopsis. The dissociation constants of 2-aminotropones were measured in 50% aqueous methanol at 20 °C and shown to be correlated by the Hammett equation with $\rho=3.40$. The difference between 4- and 6-substituents is discussed.

The dissociation constants of tropolone derivatives with a seven-membered ring structure have been reported[1] to be linearly correlated with Hammett's substituent constants. Furthermore, we have ourselves discussed[2] the Hammett relationships in the tropolone derivatives on the basis of a simple HMO method.

On the other hand, no systematic study of the dissociation of 2-aminotropones has been reported, although a few dissociation constants are known.[3]

This communication will deal with the measurements of the dissociation constants of 2-aminotropone derivatives (Fig. 1) and with their analysis by means of the Hammett relationships.

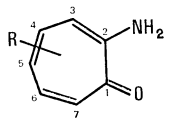

Fig. 1. 2-Aminotropones.

Results and Discussion

Dissociation Constants. The dissociation constants of 4-, 5-, and 6-substituted 2-aminotropones were determined spectrophotometrically in 50% aqueous methanol at 20 °C. The results expressed in terms of pK_a values are listed in Table 1, together with the Hammett substituent constants.[4]

TABLE 1. DISSOCIATION CONSTANTS OF 2-AMINOTROPONES

No.[a]	R	σ	pK_a
1	5-CH_3	−0.170	2.63
2	4-CH_3	−0.069	2.52
3	6-CH_3	−0.059[b]	2.36
4	6-CH=CH-Ph	−0.041[b]	2.30
5	H	0	2.16
6	4-CH=CH-Ph	0.025[c]	2.11
7	5-Cl	0.227	1.34

a) Numbering of substituents refers to that given in Fig. 2. b) Results in this work. c) Value in Ref. 8.

The 2-aminotropones show pK_a values between 2.63 (5-methyl) and 1.34 (5-chloro) and are less basic than the aniline derivatives. The pK_a values for the corresponding aniline derivatives are from 5.10 (*p*-methyl) to 3.98 (*p*-chloro).[5] This difference may be attributed to the electron-withdrawing effect of the carbonyl group adjacent to the amino group in the tropone ring.

The pK_a values for 2-amino-5-nitrotropone could not be measured, since the nitro group is a strong electron-attracting group ($\sigma_p=0.778$) and so reduced the basicity to $pK_a<1$.

Substituent Effects. When the pK_a values of 2-aminotropones are plotted against the substituent constants, the plot gives the straight line shown in Fig. 2. Here, the substituent constants, the σ_m and σ_p values, are respectively applied to the 4- and 5-positions in the tropone nucleus in the same manner as those of the tropolones.[1,2] The following equation was obtained by the least-squares method:

$$pK_a = 2.16-3.40\sigma \quad (r=0.982) \qquad (1)$$

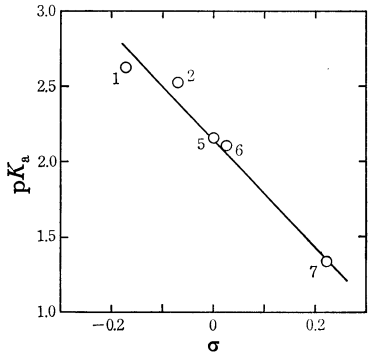

Fig. 2. The Hammett plot of pK_a.

It is of some interest to compare the ρ value obtained in the present work with those of tropolones, phenols, and anilines. The ρ value (3.40) for 2-aminotropones is comparable to that ($\rho=3.44$ in 30% ethanol at 25 °C) for anilines.[6] It has also been shown that the ρ value for tropolones ($\rho=2.68$ in water at 25 °C)[1] is comparable to that of phenols ($\rho=2.55$ in 48.9% ethanol at 20—22 °C).[7] The ratios of amino-substituted compounds to hydroxy-substituted compounds are 1.27 for troponoids and 1.35 for benzenoids. These ratios are almost equal.

4- and 6-Substituents. 4-Substituted tropolones show only one pK_a value, though they can exist in two non-equivalent tautomeric forms—as 4- and 6-substituted 2-hydroxytropones. On the other hand, 4- and 6-substituted 2-aminotropones were both obtained as pure materials, and the σ values for the 6-substituents could be estimated by using 6-substituted isomers.

The substituent constants for the 6-methyl and 6-styryl groups were estimated to be −0.059 and −0.041 respectively by using Eq. (1). The substituents in the 4- and 6-positions cannot conjugate with the

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amino group; their effect is mainly due to the inductive effect.

As regards the methyl groups, the σ_6 value (−0.059) is larger than the $\sigma_4(\equiv\sigma_m)$ value (−0.069).[4] The electron-donating effect of the 6-methyl group decreases in comparison with that of the 4-methyl group. This may be attributed to the difference in distance between the methyl group and the amino group.

The 4-styryl group (σ_m=0.025)[8] decreased the basicity of 2-aminotropone by its inductive electron-attracting effect, while 6-styryl group enhanced the basicity to pK_a=2.30. The pK_a value gave σ_6=−0.041 for the 6-styryl group in the same manner as for the 6-methyl group. The resonance of the 6-styryl group with a carbonyl adjacent to the amino group enriches the electron density of the oxygen atom. Consequently, the hydrogen bonding of hydrogen in the amino group with the carbonyl oxygen atom is enhanced and the dissociation of the ammonium ion becomes difficult. This is consistent with the difference in $\nu_{C=O}$ values of the two series of 4- and 6-styryl-2-aminotropones.[9]

Experimental

Materials. The 2-aminotropones used for the measurements of the dissociation constants were prepared by the methods described in the references.

Their melting pointed are as follows: 2-Aminotropone, mp 107—108 °C (ref.[10,11] 106—107 °C); 4-methyl-2-aminotropone, mp 124.5—125.5 °C (ref.[12,13] 122—123 °C); 5-methyl-2-aminotropone, mp 109—111.5 °C (ref.[12] 105—107 °C); 6-methyl-2-aminotropone, mp 113.5—114.5 °C (ref.[12,14] 111—112 °C); 5-chloro-2-aminotropone, mp 160.5—161.5 °C (ref.[15] 157 °C); 4-styryl-2-aminotropone, mp 194—195 °C (ref.[16] 194.5—195 °C); 6-styryl-2-aminotropone, mp 137—138 °C (ref.[16,17] 137—138 °C).

Measurements of the Dissociation Constants. The dissociation constants of 2-aminotropones were measured spectrophotometrically in 50% aqueous methanol at 20 °C by the method of Albert and Serjeant.[18]

The absorption spectra were taken on a Hitachi EPS-3T spectrophotometer, while the pH values were measured by means of a Hitachi-Horiba pH meter.

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