*Tetrahedron.* Vol. 27, pp. 337 to 340. Pergamon Press 1971. Printed in Great Britain

# SUBSTITUENT EFFECT ON DISSOCIATION CONSTANTS OF 5-(SUBSTITUTED STYRYL)TROPOLONES

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(*Received: Japan* 15 *August* 1970; *Recived in the UK for publication* 15 *September* 1970)

**Abstract**—Dissociation constants of a series of 5-styryl-tropolones were measured in 50 vol % aqueous methanol and shown to be correlated by the Hammett free energy relationship with $\rho = 0 \cdot 60$. The *π-electron densities of O-atoms and adjacent C-atoms in the 5-styryltropolones were calculated by a simple HMO method. Substituent effects in the 5-styryltropolones are compared with those in 4-styryltropolones.*

## INTRODUCTION

In a previous paper[1] it was reported that the dissociation constants of 4-styryltropolones are well correlated by the Hammett free energy relationship with $\rho = 0 \cdot 13$. In addition, the π-electron densities of O-atoms and adjacent C-atoms were calculated and plots of the π-electron densities *vs* the Hammett substituent constants roughly defined a line.

The styryl group in the 4-styryltropolones is positioned such that the resonance between the styryl group and the reaction centre of the tropolone nucleus is inhibited and, therefore, mainly an inductive effect is the governing factor in this case.

In 5-styryltropolone, on the other hand, both the resonance and inductive effects would be operating. The effect of substituents on p*Ka*'s of the 5-styryltropolones, have been compared with those in the 4-styryltropolones.

This report contains the results of a study to determine the dissociation constants, and to calculate the π-electron densities of O-atoms and adjacent C-atoms of the 5-styryltropolones (Fig 1).

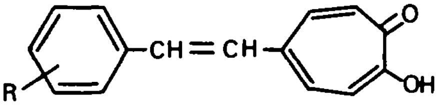

FIG. 1.

## RESULTS AND DISCUSSION

*π-Electron densities of the oxygen and adjacent carbon atoms.* The π-electron densities of the O-atoms and the adjacent C-atoms in the 5-styryltropolone were calculated by a simple HMO method and were treated in the manner described.[2] Fueno's parameters[3] were chosen for integral parameters for the substituents.

The calculated values of the π-electron densities are listed in Table 1. A plot of the π-electron densities *vs* the Hammett substituent constants appears in Fig 2. It was shown that the points form a well defined line and the slope is larger than that of the 4-styryltropolones.[1]

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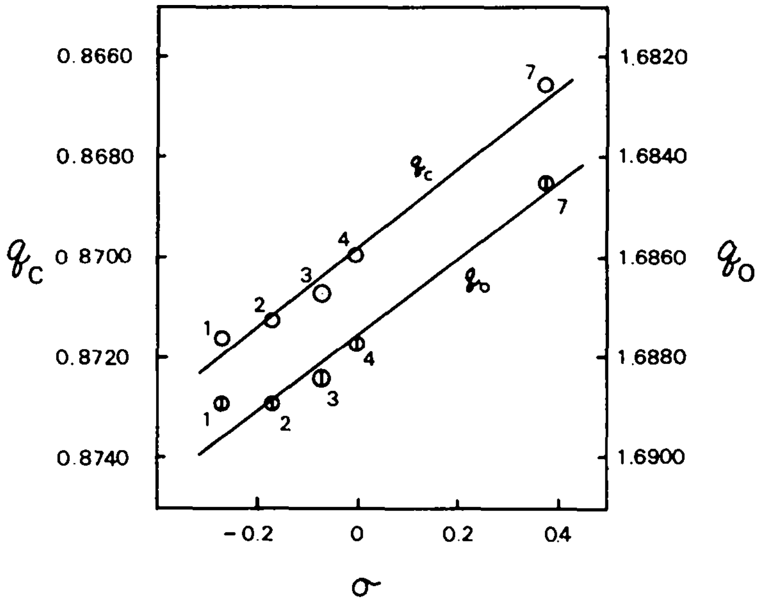

FIG. 2. The relation of π-electron densities of oxygen atoms (Φ) and adjacent carbon atoms (O) in 5-styryltropolones to substituent constants.

TABLE 1. π-ELECTRON DENSITIES OF OXYGEN ATOMS ($q_o$) AND ADJACENT CARBON ATOMS ($q_c$) OF 5-STYRYLTROPOLONES

| No. | Substituent | $\sigma^4$ | $q_c$ | $q_o$ |
|---|---|---|---|---|
| 1 | $p$-OCH$_3$ | −0·268 | 0·8716 | 1·6889 |
| 2 | $p$-CH$_3$ | −0·170 | 0·8712 | 1·6889 |
| 3 | $m$-CH$_3$ | −0·069 | 0·8707 | 1·6884 |
| 4 | H | 0·000 | 0·8699 | 1·6877 |
| 7 | $m$-Cl | 0·373 | 0·8665 | 1·6845 |

No. of substituents are referred to Fig 2.

TABLE 2. DISSOCIATION CONSTANTS OF THE 5-STYRYLTROPOLONES

| No. | Substituent | $\sigma^4$ | pKa |
|---|---|---|---|
| 1 | $p$-OCH$_3$ | −0·268 | 7·45 |
| 2 | $p$-CH$_3$ | −0·170 | 7·37 |
| 3 | $m$-CH$_3$ | −0·069 | 7·31 |
| 4 | H | 0·000 | 7·25 |
| 5 | $p$-Cl | 0·227 | 7·15 |
| 6 | $p$-Br | 0·232 | 7·11 |
| 7 | $m$-Cl | 0·373 | 7·06 |

*Dissociation constants and substituent effect.* The dissociation constants of 5-(*p*-methoxystyryl)-, 5-(*p*-methylstyryl)-, 5-(*m*-methylstyryl)-, 5-styryl-, 5-(*p*-bromostyryl)-, 5-(*p*-chlorostyryl)-, and 5-(*m*-chlorostyryl)tropolone are summarized in Table 2. When these p*Ka*'s are plotted against the Hammett substituent constants, $\sigma$, the plots defined a line as shown in Fig 3 and the following equation is obtained by the least square method.

$$pKa = 7{\cdot}27 - 0{\cdot}60\sigma$$

The fit is, by Jaffe's standard,[5] satisfactory with correlation coefficient, $r = 0{\cdot}993$, and the standard deviation, $s = 0{\cdot}01$. The reaction constant as a transmission coefficient of the substituent effects was found to be 0·60.

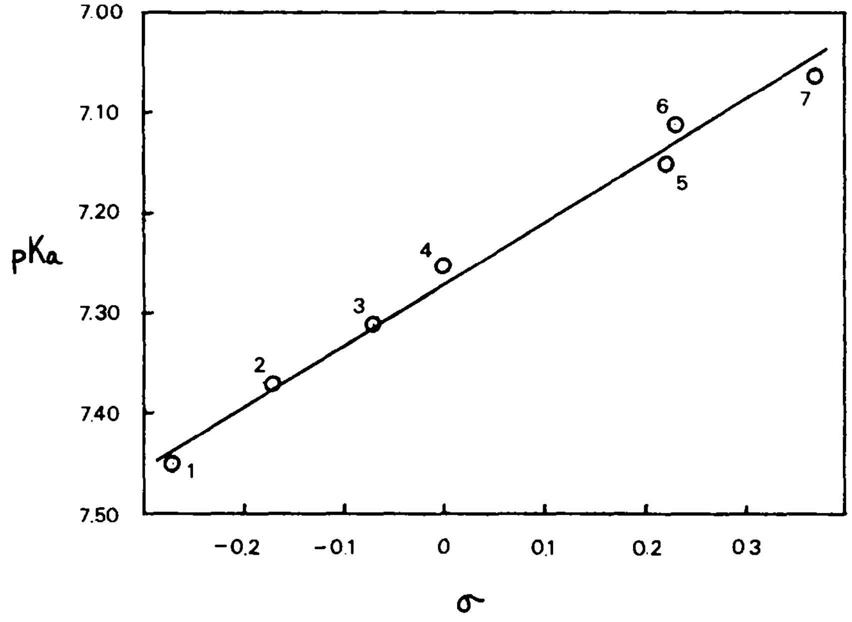

FIG. 3. The correlation of pKa's of *p*-styryltropolones with substituent constants.

*Reaction constant.* The reaction constant, $\rho = 0{\cdot}60$, is larger than the expected value (0·2–0·3)[1] which was estimated from the ratio of the reaction constants of 3- and 4-styrylpyridines (0·44[6] and 0·85[7], respectively), and the reaction constant of 4-styryltropolone (0·13).[1] Both tautomeric forms—2-hydroxy-4-styryltropone and 2-hydroxy-6-styryltropone—can contribute to the p*Ka*, whereas only one reaction centre is involved in the styrylpyridines. The dissociation constant of the 4-styryltropolone is, therefore, the combination of two non equivalent tautomeric forms corresponding to the different UV spectra of 4- and 6-substituted styryltropolone methyl ethers[8] and the substituent effects should vary in these two forms. Consequently, it would be inadequate to use the ratio of the reaction constants of 3- and 4-styrylpyridines for the estimation of $\rho$ value of the 5-styryltropolone. 5-Styryltropolone, on the other hand, has almost identical tautomeric forms as the styryl group is located at a symmetrical position of the tropolone nucleus. This indicates that the contribution of each tautomeric form to the p*Ka* is practically equal.

The ratio of the slopes of the line, obtained from the diagrams of the $\pi$-electron densities at the C-atoms adjacent to the O-atoms *vs* the Hammett substituent constants in 4-and 5-styryltropolones is 4·70, which is nearly the same as the ratio of the reaction constants, 4·62, obtained in our experiments.

## EXPERIMENTAL

*Materials.* 5-Styryltropolones were obtained by the Wittig reaction of 5-formyltropolone with substituted benzylidene triphenylphosphonium ylids.[9] The compounds were recrystallized from benzene or from a mixture of benzene–light petroleum.

*Measurement of the dissociation constants.* The dissociation constants of the 5-styryltropolone in 50% MeOH were determined spectroscopically using a Hatachi-Horiba F–5 pH meter. The measurements were carried out at 20°.

*Acknowledgements*—We wish to thank the Ministry of Education for the support by a grant (1968–1970).

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