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SUBSTITUENT EFFECT ON DISSOCIATION CONSTANTS OF 4-(SUBSTITUTED STYRYL)TROPOLONES

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Abstract—Dissociation constants of a series of 4-styryltropolones were measured in 50 volume per cent aqueous methanol and shown to be correlated by the Hammett free energy relationship with $\rho = 0{\cdot}13$. The π-electron densities of O-atoms and neighboring C-atoms in the 4-styryltropolones were calculated by a simple HMO method. Substituent effects in the 4-styryltropolones are discussed briefly.

INTRODUCTION

4-STYRYLTROPOLONE methyl ether reacts with various nucleophilic reagents such as guanidine[1] and thiourea[2] to give ring formation products, but does not react with urea, like other troponoids. However, 4-(*p*-nitrostyryl)tropolone methyl ether reacts not only with guanidine and thiourea but also with urea to afford condensed-ring compounds.[3] This seems to indicate that a substituent in the benzene ring influences the reactivity of the tropolone nucleus. These substituent effects have been studied in a more quantitative manner by correlating the dissociation constants and the π-electron densities of the O-atoms and the adjacent C-atoms of 4-styryltropolones, with Hammett substituent constants. For this purpose, 4-(*p*-methylstyryl)-, 4-(*p*-chlorostyryl)-, 4-(*m*-chlorostyryl)-, and 4-(*m*-nitrostyryl)tropolones were synthesized.

RESULTS AND DISCUSSION

π-Electron densities of the oxygen and adjacent carbon atoms. The π-electron densities of the O-atoms and C-atoms in the 4-styryltropolones were calculated by a simple HMO method and were treated in the same manner described.[4] Fueno's parameters[5] were chosen for integral parameters for the substituents.

The calculated values of the π-electron densities are listed in Table 1. The Hammett type analysis of the values obtained was fairly successful. In this case a plot of the π-electron densities *vs* Hammett substituent constants appears in Fig 1. It will be seen that the points roughly define a line. The slope, however, is very small and this is due to the fact that the substituents are located at a position far distant from the O and C-atoms concerned.

Dissociation constants and substituent effect. The dissociation constants of 4-(*p*-methylstyryl)-, 4-styryl-, 4-(*p*-chlorostyryl)-, 4-(*m*-chlorostyryl)-, and 4-(*m*-nitrostyryl)tropolones are summarized in Table 2. When these pK_a's are plotted against the substituent constants, the plot well defines a line as shown in Fig 2, and the following equation is obtained by the least square method.

$$pK_a = 7{\cdot}83 - 0{\cdot}13\sigma$$

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TABLE 1. π-ELECTRON DENSITIES OF OXYGEN ATOMS (q_O) AND ADJACENT CARBON ATOMS (q_C) OF 4-STYRYLTROPOLONES

No.	Substituent	σ	q_C	q_O
1	p-CH_3	−0·170	0·8755	1·6990
2	H	0·000	0·8751	1·6987
3	m-Cl	0·373	0·8744	1·6980

No. of substituents are referred to Fig. 1.

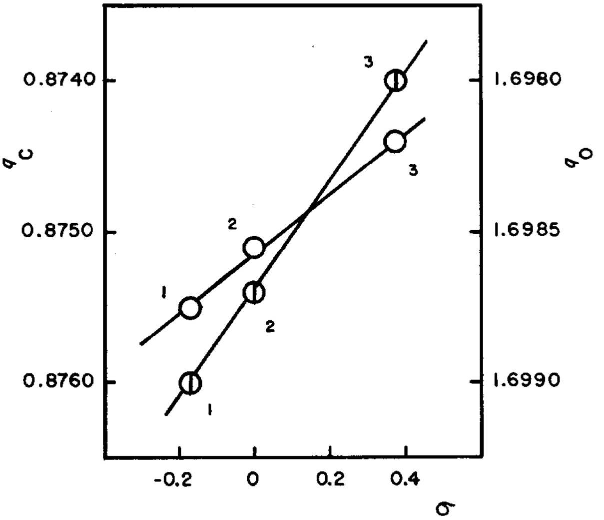

FIG. 1 The relation of π-electron densities of oxygen atoms (⦶) and adjacent carbon atoms (○) to substituent constants.

The fit is, by Jaffé's standard, satisfactory, with correlation coefficient, $r = -0{\cdot}969$ and standard deviation, $s = 0{\cdot}01$. The reaction constant as a transmission coefficient of the substituent effects was found to be 0·13.

As the Hammett substituent constants, σ, are assumed to represent as average blend of inductive and resonance effects of these substituents, one would expect any inductive contribution to σ constants to decrease rapidly with increasing distance. The resonance contribution, on the other hand, would be expected to be less sensitive to distance. However, the resonance contribution can be ignored in our case as the styryl

TABLE 2. DISSOCIATION CONSTANTS OF 4-STYRYLTROPOLONES

No.	Substituent	σ	pK_a
1	p-CH_3	−0·170	7·85
2	H	0·000	7·83
•3	p-Cl	0·227	7·81
4	m-Cl	0·373	7·76
5	m-NO_2	0·710	7·74

No. of substituents are referred to Fig. 2.

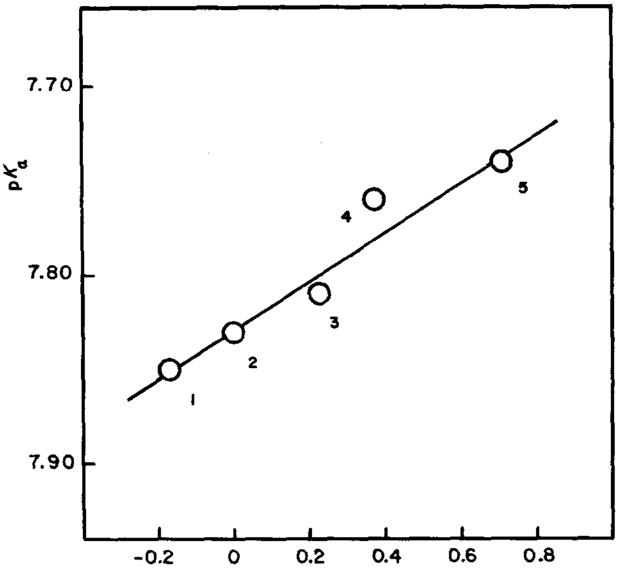

FIG. 2 The correlation of pK_a's with substituent constants.

group is located at such a position that the resonance between the styryl group and the reaction center of the tropolone nucleus is inhibited.

Reaction constant. It is some of interest to compare the value of the reaction constant, ρ, obtained in the present work with those of tropolones,[6] pyridines,[7] 3-styrylpyridines,[8] and 4-styrylpyridines.[9] They are listed in Table 3 and show that the reaction constant, ρ = 0·13 for 4-styryltropolones is about one tenth of that for tropolones, ρ = 2·68. This is also shown in the cases of 3-styrylpyridines (ρ = 0·44) and pyridines (ρ = 5·71). In these systems where resonances are not allowed between a styryl group and a reaction centre of a tropolone or pyridine nucleus, only the inductive effect is the governing factor for the reaction constant.

It seems reasonable that the rate-retarding factor for *m*-styryl group is about ten, when it is compared with that of a phenyl group which is well known to exhibit a –I effect and various authors have ascribed a rate-retarding factor of 8 to 10 to this depressive effect for a phenyl group.

It is also possible to estimate a reaction constant in the dissociation of 5-styryl-

TABLE 3. REACTION CONSTANTS IN DISSOCIATIONS

Series of compds	ρ	Ref
Tropolones	2·68	6
4-Styryltropolones	0·13	*a*
Pyridines	5·71	7
3-Styrylpyridines	0·44	8
4-Styrylpyridines	0·85	9

a. Result in this work.

tropolones as 0·2 to 0·3. This was calculated from the ratio of the reaction constants of the 3- and 4-styrylpyridines and that of the 4-styryltropolones. Studies on 5-styryltropolones are now in progress.

EXPERIMENTAL

Materials. 4-(*p*-Methylstyryl)-, 4-(*p*-chlorostyryl)-, 4-(*m*-chlorostyryl)-, and 4-(*m*-nitrostyryl)tropolones were synthesized[10] in a manner similar to the preparation of 4-styryltropolone.[11] The corresponding aldehydes were treated with 3-carboxy-4-carboxymethyltropolone[12] which was obtained from purpurogallin[13] by sodium periodate oxidation, to give 3-carboxy-4-styryltropolones. 3-Carboxy-4-styryltropolones were sublimed at elevated temperature to afford 4-styryltropolones with the loss of carbon dioxide. The 4-styryltropolones were purified by repeated crystallization from methanol. Their m.ps and analytical data are listed in Table 4.

TABLE 4. 4-(SUBSTITUTED STYRYL)TROPOLONES

Substituent	Mp.	Analysis					
		Found			Calc.		
	°C	C %	H %	N %	C %	H %	N %
H	90–90·5[a]						
p-CH_3	156–156·5	80·34	5·90		80·64	5·92	
p-Cl	151–151·5	69·57	4·28		69·62	4·26	
m-Cl	138·5–139	68·98	4·27		69·62	4·26	
m-NO_2	142–143	66·74	4·06	5·19	66·91	4·12	5·20

[a] Mp. 90·5–91° (Ref. 11).

Measurement of the dissociation constants. The dissociation constants of the 4-styryltropolones in 50 volume per cent aqueous MeOH were determined spectroscopically by using a Hitachi Model EPS-2 spectrophotometer. pH's were measured on a Hitachi-Horiba F-5 pH meter. The measurements were performed at 20°.

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