Cooling of the aqueous filtrate yielded 0.3 g (30%) of 3-phenylthiocarbamoylthiazolidine-2,4-dione VI with mp 155-156°. Found: C 47.8; H 3.2; N 10.8%; M 229 (in mass-spectrum). C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>. Calculated: C 47.6; H 3.2; N 11.1%; M 232. Evaporation of the hydrochloric acid filtrate gave 0.38 g (38%) of 3-phenyl-thiazolidine-2,4-dione III with mp 142-143° (no melting-point depression was observed for a mixture of this product with the product obtained by the method in [3]). The hydrochloric acid filtrate was neutralized with 10% Na<sub>2</sub>CO<sub>3</sub> solution, saturated with alkali, and extracted with ether. The ether extract was treated with a mixture of acetic acid and acetic anhydride and the mixture was worked up to give acetanilide, with mp 114° (from water), which was identified by a mixed-melting point determination.

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## HAMMETT CONSTANTS OF THE PYRROLINE-2,5-DIONE RING

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The electronic effect of the pyrroline-2,5-dione ring on the benzene ring in the case of N-aryl compounds is close to the effect exerted by halogens. The overall electron-acceptor effect depends markedly on the nature of the solvent. The electron-donor effect of conjugation is small.

In the present paper we have made a quantitative evaluation of the electronic nature of the pyrroline-2,5-dione (maleinimide) and pyrrolidine-2,5-dione rings within the framework of the Hammett-Taft method.

In conformity with this, we determined the  $\sigma$  constants of pyrroline-2,5-dion-1-yl (I), pyrrolidine-2,5-dion-1-yl (II), and 3-chloropyrrolidine-2,5-dion-1-yl (III) substituents for the para ( $\sigma_p$ ) and meta ( $\sigma_m$ ) positions with respect to the ionization of p- and m-substituted benzoic acids and, on the basis of the results, estimated, from the Taft equations, the independent contributions and the magnitudes of the substituent constants of the inductive ( $\sigma_i$ ) and conjugation ( $\sigma_c$ ) effects. The  $\sigma_i$  and  $\sigma_c$  constants found were compared with the corresponding constants calculated on the basis of the F<sup>19</sup> NMR chemical shifts in the spectra of p- and m-substituted fluorobenzenes.

The information obtained may be of interest in connection with the fact that in recent years maleinimides have received widespread recognition as subjects for the investigation of the chemistry of heterocyclic chain polymers [1].



The  $\sigma$  constants of substituents I-III in the equation

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$$|g \frac{k}{k_0} = \rho \cdot \sigma \tag{1}$$

were found with respect to the ionization of p- and m-substituted benzoic acids in 50% aqueous ethanol at  $25^{\circ}$ C. The reaction constant for the indicated conditions was assumed to be 1.535 [2]. and the dissociation constant of unsubstituted benzoic acid was assumed to be 5.71 [3]. The investigated acids are stronger than benzoic acid, and the electron-acceptor properties of the rings of I-III are less expressed when they are in the para position than when they are in the meta position; this is characteristic for substituents that have opposite inductive and conjugation effects. The  $\sigma$  constants of the substituents calculated from Eq. (1) are presented in Table 1 along with the results of separation of the Hammett constants into independent contributions of the inductive and conjugation effects from Taft equations (2) and (3) [4]:

$$\sigma_{i} = \frac{1}{\rho_{i}(1-\alpha)} \lg \frac{k_{m}}{k_{o}} - \lg \frac{k_{p}}{k_{o}}, \qquad (2)$$

$$\sigma_c = \frac{1}{\rho_i} \lg \frac{k_p}{k_o} - \sigma_i, \tag{3}$$

where  $k_m$ ,  $k_p$ , and  $k_0$  are, respectively, the ionization constants of m- and p-substituted benzoic acid and unsubstituted benzoic acid,  $\rho_i$  is the reaction constant for the inductive effect, and  $\alpha$  is a constant that depends on the type of reaction. In our calculations the  $\rho_i$  and  $\alpha$  values were assumed to be 1.50 and 0.42, respectively [5].

Considering the high tendency of the oxygen atom of the carbonyl groups of the rings of I-III to form hydrogen bonds with proton-donor solvents, it must be noted that the  $\sigma$ ,  $\sigma_i$ , and  $\sigma_c$  constants calculated from Eqs. (1)-(3) characterize the investigate substituents in the state of solvation, which, as one might assume, increases their electron-acceptor character due to intensification of the  $\sigma$ , $\pi$ -accepting effect of the carbonyl groups.

In this connection, it seemed of interest to compare the Taft constants calculated from reactivity data with the analogous values calculated on the basis of the  $F^{19}$  NMR chemical shifts in the spectra of p- and m-substituted fluorobenzenes, which, it is well known, quite accurately reflect the effect of a substituent on the electronic system of the benzene ring via an inductive mechanism and the conjugation effect [6]. With this end in mind, we investigated the  $F^{19}$  NMR spectra of m- and p-substituted fluorobenzenes with substituents I-III in dichloroethane solutions and calculated the Taft constants from Eqs. (4) and (5) (Fig. 1 and Table 1):

$$\delta_{\rm m} = -7.1\sigma_{\rm i} + 0.6,$$
 (4)

$$\delta_{\rm p} = \delta_{\rm m} - 29.5\sigma_{\rm c},\tag{5}$$

where  $\delta_m^F$  and  $\delta_p^F$  are the chemical shifts of the fluorine nuclei in m- and p-substituted fluorobenzenes reckoned from the signal of unsubstituted fluorobenzene and expressed in parts per million of the resonance frequency; positive  $\delta$  values indicate an increase in the shielding of the fluorine nuclei.

We also estimated the constants of the pyrroline-2,5-dione ring from the shift of the band of the OH stretching vibrations in the spectrum of 1-(4-hydroxyphenyl)pyrrolidine-2,5-dione relative to the analogous band in the spectrum of unsubstituted phenol in  $CCl_4$  solution. The II and III substituents cannot be similarly investigated because of the low solubility of 1-arylpyrrolidine-2,5-diones in nonpolar organic solvents.

The analysis of the correlation of the  $\sigma$  substituent constants with the shifts of the vibrational frequencies  $(\Delta\nu_{OH})$  in the spectra of p-substituted phenols carried out in [7] constitutes evidence that the latter fit extremely well on the correlation line  $\sigma = -0.0645 \Delta\nu_{OH}$ . This dependence makes it possible to estimate the  $\sigma$  constant of the pyrrolidine-2,5-dione ring  $(\Delta\nu_{OH} = -3.5 \text{ cm}^{-1})$  as  $0.23 \pm 0.03$  for a confidence probability of 0.95.

TABLE 1.  $\sigma$  Substituent Constants and pK<sub>a</sub> Values of m- and p-Substituted Benzoic Acids and F<sup>19</sup> Chemical Shifts in the Spectra of mand p-Substituted Chlorobenzenes

Substituent	meta position			para position			σi		σ <sub>c</sub>	
	₽K a	۳m	δ <sub>m</sub> , ppm	pK <sub>a</sub>	۳p	<sup>δ</sup> p, ppm	from pK <sub>a</sub>	from NMR	from pK <sub>a</sub>	from NMR
Pyrroline-2,5-dion-	5,21	0,326	- 1.65	5.30	0.267	+0,494	0,377	0,317	-0,110	0,073
Pyrrolidine-2,5-dion-	5,19	0,339	-1,55	5,23	0,313	-0,200	0,366	0.303	-0,053	-0,046
1-yl 3-Chloropyrrolidine- 2,5-dion-1-yl	4,99	0,469	-2,15	5,01	0,456	-1,320	0,489	0,387	-0.032	-0,028



Fig. 1. F<sup>19</sup> NMR spectra in dichloroethane (2.5 mole %) at 80 MHz [the chemical shifts are indicated in parts per million relative to hexafluorobenzene (the internal standard)]: a) 1-(p-fluorophenyl)pyrroline-2,5-dione; b) 1-(p-fluorophenyl)pyrrolidine-2,5-dione; c) 1-(p-fluorophenyl)-3-chloropyrrolidine-2,5-dione; d) 1-(m-fluorophenyl)pyrroline-2,5dione; e) 1-(-fluorophenyl)pyrrolidine-2,5-dione; f) 1-(mfluorophenyl)-3-chloropyrrolidine-2,5-dione.

The calculated  $\sigma$  constants presented in Table 1 show that the electron-acceptor character of substituents I-III is due to a negative inductive effect, whereas the electron-donor effect of conjugation in the ground state is small. The results are in good agreement with the results of a calculation of the electron density distribution in pyrrolidine-2,5-dione and 1-phenylpyrrolidine-2,5-dione molecules by the Pariser-Parr-Pople method [8].

The  $\sigma$  constants found from the reactivities are somewhat higher than the values calculated from NMR data and, as already noted, this is probably associated with a change in the electronic state of the substituents under the influence of the medium. The overall perturbation effect of diacylated nitrogen included in a fivemembered ring is close to the effect exerted on the benzene ring by halogens (for Br:  $\sigma_i = 0.44$  and  $\sigma_c = -0.16$ ) [9]. In analogy with the latter, despite the overall electron-acceptor character, the pyrrolidine-2,5-dione ring in the case of N-aryl addition in electrophilic aromatic substitution reactions is an ortho, para-orientation, as follows from data on the chlorosulfonation of 1-phenylpyrrolidine-2,5-dione [10]. The ortho, para-orientating effect of the ring is probably due to partial migration, under the influence of a strong electrophilic agent, of the free electron pair of nitrogens, which is delocalized in the ground state primarily on the carbonyl groups, to the benzene ring and to the formation in the transition state of a more stable p-substituted carbonium ion as compared with the m-substituted compound. However, as a consequence of the fact that the effect of de-localization of the free electrons of nitrogen on the carbonyl group is competitive with respect to the effect of polar conjugation in the carbonium ion, one cannot exclude the possibility that primarily meta orientation will be observed in electrophilic aromatic substitution reactions with the participation of weaker electrophilic agents.

A comparison of the Taft constants in the series of substituents NHCOCH<sub>3</sub> ( $\sigma_i = -0.26$ ,  $\sigma_c = 0.20$ ) [9], II, and III makes it possible to conclude that there is no "saturation" effect of carbonyl groups on the sensitivity of nitrogen to the electron-acceptor effect, particularly to electron-acceptor substituents attached to the C (3) and C (4) ring atoms.

On passing from substituent I to II, the change in the hybridization in the ring C  $_{(3)}$  and C  $_{(4)}$  ring atoms leads to weakening of the inductive component of the overall effect, but in this case the  $\pi$ -accepting effect of the oxygen atoms of the carbonyl groups on the imide nitrogen atom increases substantially; this is manifested as a decrease in the conjugation of the latter with the benzene ring. As a result, the overall electron-acceptor effect of the pyrrolidine-2,5-dione ring on the benzene ring turns out to be higher in the case of N-aryl addition than in the case of pyrroline-2,5-dione addition.

Finally, since a linear dependence between the conjugation constant and the bond order is satisfactorily observed for the  $>N-C_{ap}$  system [11], by comparing  $\sigma_c$  for substituents I-III one may arrive at the conclusion that the strength characteristics of the  $C_6H_5-N$  bond decrease in the order III > II > I.

## EXPERIMENTAL

The ionization constants of m- and p-substituted benzoic acids were determined by potentiometric titration with a glass electrode [12] at 25° of 0.01 M solutions of the acids in 50% (by volume at the half-neutralization point) aqueous ethanol with a 0.1 M solution of potassium hydroxide free of carbonate. The reproducibility of the pKa value of benzoic acid under our conditions was  $5.70 \pm 0.02$  (as compared with 5.71 [3]). The measurements were made with a pH-340 pH-meter. Prior to the pKa measurements, the acids were purified by two crystallizations and were stored in a vacuum desiccator.

The  $F^{19}$  NMR spectra of the compounds in dichloroethane were recorded with a Tesla BS 487B spectrometer at 80 MHz. The concentration of the working solutions was 2.5 mole %. The chemical shifts of the Fnuclei in chlorobenzene and its substituted derivatives were measured in accordance with the recommendation of Emsley and Phillips [13] relative to hexafluorobenzene, which was added in 100 mole % amounts to the investigated substances. Conversion of the chemical shifts relative to hexafluorobenzene to the position of the signal from unsubstituted benzene was carried out for the signal from fluorine. The signal from unsubstituted fluorobenzene (2.5 mole % in dichloroethane) was found at weaker field (by 49.03 ppm) relative to the signal from hexafluorobenzene. The chemical shifts (Fig. 1) presented in Table 1 are expressed in the following units:

$$\delta = 49.03 \text{ ppm} - \frac{\Lambda_i^2}{80.0}$$

where  $\Delta f$  is the distance expressed in Hertz between the investigated signal and the signal of hexafluorobenzene. Negative  $\delta$  values correspond to the location of a signal at weaker field than the signal from fluorobenzene.

The IR spectra of phenol and its p-substituted (methyl, chloro, bromo, iodo, methoxy, and nitro) derivatives were measured with a UR-20 spectrometer in a NaCl cuvette at an absorbing layer thickness of 100 mm for  $5 \cdot 10^{-4}$  mole/liter solutions of the compounds in CCl<sub>4</sub>. The results were processed as in [7].

<u>1-(p-Fluorophenyl)pyrroline-2,5-dione</u>. A solution of 22.2 g (0.2 mole) of p-fluoroaniline in 50 ml of acetone was added to 20.6 g (0.21 mole) of maleic anhydride in 150 ml of acetone. After 2 h, the N-(p-fluorophenyl)maleinamic acid was separated by filtration to give 37.6 g (90%) of a product with mp 187.5-189°. A 20.9-g (0.1 mole) sample of this acid was heated with 20 g of anhydrous sodium acetate and 102 g (1.0 mole) of acetic anhydride at 80° for 20 min in a flask with a reflux condenser and a stirrer. The mixture was then poured over ice, and the resulting precipitate was washed thoroughly on the filter with water to give 16 g (84%) of lemon-colored needles with mp 154.5-155° (from benzene—heptane). Found: N 7.30%.  $C_{10}H_6FNO_2$ . Calculated: N 7.33%.

<u>1-(m-Fluorophenyl)pyrroline-2,5-dione</u>. This compound, with mp 54-55° (from hexane), was similarly synthesized from m-fluoroaniline and was obtained in 79% yield. Found: N 7.29%.  $C_{10}H_6FNO_2$ . Calculated: N 7.33%.

<u>1-(p-Fluorophenyl)pyrrolidine-2,5-dione</u>. This compound, with mp 163-164° (from toluene-hexane), was obtained by reduction of 3.8 g (0.02 mole) of 1-(p-fluorophenyl)pyrroline-2,5-dione with zinc dust in acetic acid at 60° for 40 min. The yield was 2.6 g (68%). Found: N 7.20%.  $C_{10}H_8FNO_2$ . Calculated: N 7.25%.

<u>1-(m-Fluorophenyl)pyrrolidine-2,5-dione</u>. This compound, with mp 106-107° (from toluene-hexane), was obtained in 70% yield from 1-(m-fluorophenyl)pyrroline-2,5-dione by the method used to prepare the para isomer. Found: N 7.26%.  $C_{10}H_8FNO_4$ . Calculated: N 7.25%.

1- (p-Fluorophenyl)-3-chloropyrrolidine-2,5-dione. A 3.8-g (0.02 mole) sample of 1- (p-fluorophenyl)pyrroline-2,5-dione was dissolved in 50 ml of glacial acetic acid, and a gentle stream of dry hydrogen chloride was bubbled through the solution at 80° for 2 h. The mixture was then allowed to stand at room temperature for 3 h, after which it was diluted with water and worked up to give 3.2 g (71%) of a product with mp 146-148° (from hexane). Found: N 6.0%.  $C_{10}H_7CINO_2$ . Calculated: N 6.15%.

<u>1-(m-Fluorophenyl)-3-chloropyrrolidine-2,5-dione</u>. This compound, with mp 98-99° (from hexane), was obtained in 72% yield from 1-(m-fluorophenyl)pyrroline-2,5-dione by the method used to prepare the para isomer. Found: N 6.10%.  $C_{10}H_7FC1NO_2$ . Calculated: N 6.15%.

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4,9-DIHYDROBENZ[f]INDOLE-4,9-DIONE DERIVATIVES SYNTHESIS AND PROPERTIES OF 2,3,4,9-TETRAHYDROBENZ[f]INDOLE-2,4,9-TRIONES AND 2,3,4,9-TETRAHYDROBENZ[f]INDOLE-2,3,4,9-TETRONES

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Under the influence of amines, (3-chloro-1,4-naphthoquinon-2-yl)malonic ester is cyclized to 3-carbethoxy derivatives of 2,3,4,9-tetrahydrobenz[f]indole-2,4,9-trione, which were decarboxylated and then oxidized to 2,3,4,9-tetrahydrobenz[f]indole-2,3,4,9-tetrone derivatives. Methylation of 2,3,4,9-tetrahydrobenz[f]indole-2,4,9-triones leads to a mixture of O- and C-methyl derivatives.

It is known [1] that diethyl (3-bromo-1,4-naphthoquinon-2-yl)malonate is cyclized under the influence of ethylamine to ethyl 1-ethyl-2,3,4,9-tetrahydrobenz[f]indole-2.4,9-trione-3-carboxylate. This is one of the few examples [1-3] of the synthesis of benz[f]indole-4,9-quinone derivatives, whereas they are of interest for the synthesis of indigoid dyes.

We have synthesized a number of benz[f]indole-4.9-quinone derivatives and have investigated some of the physical and chemical properties of these compounds.

Ethyl 2,3,4,9-tetrahydrobenz[f]indole-2,4,9-trione-3-carboxylate (IIa) and its N-substituted derivatives (IIb-d) are obtained in good yields by reaction of (3-chloro-1,4-naphthoquinon-2-yl)malonic ester (I) with ammonia and amines. 3-Chloro-2-R-amino-1,4-naphthoquinones (where R is the corresponding amine residue) is formed as a side product in 2-10% yield; the formation of the latter is expressly a side reaction, but it is not due to a 2,3-dichloro-1,4-naphthoquinone impurity in starting I. Kitasato and Sone [2] isolated a side product, to which they assigned the (3-bromo-1,4-naphthoquinon-2-yl)acetic acid methylamide structure, when they carried out the reaction of (3-bromo-1,4-naphthoquinon-2-yl)malonic ester with methylamine. We have found that this side product is actually identical to 3-bromo-2-methylamino-1,4-naphthoquinone [4].

Our proposed method for the synthesis of IIa gives the desired product in higher overall yields and has fewer steps than the methods described in [3].

2,3,4,9-Tetrahydrobenz[f]indole-2,4.9-trione (IIIa) and its N-substituted derivatives (IIIb-d) are formed by treatment of IIa-d with boiling acetic acid.

Compounds IIa-d and IIIa-d are soluble in cold aqueous solutions of bases to give blue-violet enolates. The starting materials are regenerated when the solutions are acidified.

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