TRANSMISSION OF ELECTRONIC EFFECTS THROUGH FURAN AND THIOPHENE RINGS

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The transmissive factors for the furan and thiophene rings were calculated using statistical parameters obtained by the correlation of half-wave potentials with σ constants of the substituents. By comparison of the calculated values of the π' coefficients and by comparison of these values with that for the benzene ring, it was found that the ability to transfer the effects of substituents of the studied heterocycles decreases in the series furan > thiophene > benzene.

The results of a great number of polarographic papers devoted to studying the influence of substituents on different reaction centres in furan and thiophene rings are summarized by Zuman[1]. Although the obtained results and their comparison with benzene analogues showed that these heterocycles have similar properties to benzene, nevertheless oxygen and sulphur partially influence the reaction centres of individual systems of compounds containing these cycles. Because the published studies are devoted to the influence of substituents bound directly to the furan and thiophene rings on which the reaction centre is also placed, it was not possible to study the inhibiting effects of the heteroatoms and to calculate the transmissive factors π' for these heterocycles. Only the ratio of the reaction constants ($\varrho_{hel}/\varrho_{benz}$) for the individual series was obtained; the results showed that these values are higher for furan analogues than for thiophenes[1].

The present work deals with the study of the transmission of electronic effects of the substituents through furan and thiophene rings in the series of substituted 5-(X-phenyl)-2-furaldehydes (*Ia*), 5-(X-phenyl)-2-thiophenecarboxaldehydes (*Ib*), substituted 1-phenyl-3-[5-(X-phenyl)-2-furyl]-propen-1-ones (*IIa*) and 1-phenyl-3-[5-(X-phenyl)-2-thienyl]-propen-1-ones (*IIb*).
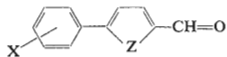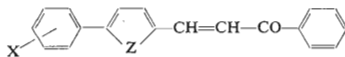
In formulae *I* and *II*   *a* Z = O
                           b Z = S

The obtained results were compared with works in which the transmissive factors were calculated using IR data of corresponding systems[2,3] and of other systems containing furan and thiophene rings[4]. The experimentally determined values of π' are further compared with the calculated values of the respective heterocycles[2,4].

EXPERIMENTAL

Apparatus. Polarographic curves were recorded with the polarograph OH-102 (Radelkis, Budapest) using a modified Kalousek cell with a separated s.c.e. At $h = 60$ cm, the dropping mercury electrode had a mercury flow rate, $m = 1.9$ mg s^{-1} and a drop time, $t_1 = 3$ s (in 0.1M-KCl at 0.0 V). The pH values of the polarographed solutions were measured with the aid of the pH-meter PHM-26 (Radiometer, Copenhagen) using the glass electrode G 202 B and the s.c.e. type K-400. The $E_{1/2}$ values of the studied compounds were measured with an accuracy of ± 2 mV with the aid of the QTK compensator (Metra, Blansko) using a three-electrode system and referred to the nonpolarizable s.c.e. The linear correlation parameters were calculated from the statistical relations[5] using the computer Hewlett Packard 9100 B.

Chemicals. The studied derivatives of the series *Ia, Ib* were prepared using modified Meerwein's methods[6,7]. The furan and thiophene rings containing chalcones (series *IIa, IIb*) were prepared by the condensation of the corresponding aldehydes (*Ia, Ib*) with acetophenone[8,9]. Before use the compounds were purified by crystallization from the corresponding solvents and the purity was tested by the determination of physical constants. Other chemicals used for the preparation of stock solutions were p.a. (Lachema, Brno).

Working conditions. 0.5 mM ethanol solutions of all derivatives were prepared. These solutions were mixed with Britton-Robinson buffer solutions in a ratio such that the resulting concentration of the depolarizator was 0.1 mM and the resulting concentration of ethanol was 50% in the polarographed solution. The $E_{1/2}$ values used for the correlations were measured for series *I* and *II* at pH 12 and 2.6 respectively. The measurements were carried out at 20°C. Oxygen was removed from the polarographed solutions with purified nitrogen which was bubbled for 10 min through these solutions.

RESULTS AND DISCUSSION

At the dropping mercury electrode the examined derivatives of the studied series behave similarly to the corresponding benzaldehydes and chalcones. In alkaline medium, pH $\sim$ 12, the aldehydes yield a one-electron wave[10] and chalcones and their analogues yield one-electron waves[11,12] at pH <4.

These findings were used in the measurement of the $E_{1/2}$ values which are presented in Table I for the individual derivatives of the studied series. The aldehydes with thiophene rings have an $E_{1/2}$ value 50−70 mV more positive and the chalcone derivatives 30−50 mV more positive than their corresponding furan derivatives. These phenomena point out the higher conjugation and polarization of reaction centres of thiophene derivatives studied in these and similar systems[4,13].

Although the reduction mechanism of the derivatives in the studied series is similar to that of benzene analogues and is not essentially influenced by the heterocycles,

we nonetheless turned our attention to statistical evaluation of the dependence of the $E_{1/2}$ values on the σ constants of the substituents[14]. Good linear dependences for individual series were found in the pH regions where the $E_{1/2}$ values were measured. The parameters of these correlations are presented in Table II. The comparison of the determined $\varrho_{\pi,R}$ values of the studied series with their benzene analogues showed that these values are higher for benzaldehydes and chalcones. From these findings it follows that the influence of the substituents on the reaction centers of the corresponding furan and thiophene derivatives is substantially lower. From the values of the transmissive factors π' (Table II) calculated according to the relation

$$\pi'_{\text{Fu,Thio}} = \varrho_I/\varrho_a = \varrho_{II}/\varrho_{\text{ch}},$$

where ϱ_I and ϱ_{II} are the slopes of the studied series, can be seen the degree to which these heterocycles influence the transfer of the substituent electron effects. The quantities ϱ_a, ϱ_{ch} are the values of the slopes of the linear $E_{1/2} - \sigma$ correlations for the substituted benzaldehydes[15] ($\varrho_a = 0.296 \pm 0.016$) and chalcones[12] ($\varrho_{\text{ch}} = 0.106 \pm 0.002$), which were used for the calculation of the transmissive factors.

Relatively good agreement can be found by comparison of the π' values determined by us with the values obtained from the IR spectra[2-4]. The average values of the determined transmissive factors are higher for individual heterocycles ($\pi'_{\text{Fu}} = 0.65 \pm 0.05$; $\pi'_{\text{Thio}} = 0.54 \pm 0.07$) than the calculated values ($\pi'_{\text{Fu}} = 0.48$ and $\pi'_{\text{Thi}} = 0.47$), but still correspond to the proposal that the dependence of π' on the delocali-

TABLE I

$E_{1/2}$ Values of the Studied Derivatives and the Corresponding σ Constants of the Substituents

X	σ	Series, $(-E_{1/2}, \text{V})$			
		Ia	IIa	Ib	IIb
4-OH	−0.37	—	—	—	0.526
4-NHOH	−0.34	—	0.582	—	—
4-OCH$_3$	−0.27	1.469	0.570	1.396	0.530
4-CH$_3$	−0.17	1.454	0.567	1.370	0.524
3-CH$_3$	−0.07	—	—	1.368	0.524
3-NHOH	−0.04	1.428	—	—	—
H	0.00	1.413	0.548	1.355	0.508
4-Cl	0.23	1.380	0.535	1.308	0.495
4-Br	0.23	1.377	0.539	1.315	0.500
3-F	0.35	1.362	—	—	—
3-Cl	0.37	0.354	0.524	1.300	0.488
3-Br	0.39	1.348	0.527	—	—

TABLE II

Statistical Parameters of the Linear Dependences for the Studied Series and Transmissive Factors for the Furan and Thiophene Rings

Symbols: n number of derivatives used for the correlation, $\varrho_{\pi,R}$ slope, $E_{1/2}^0$ theoretical value of non-substituted derivative, r correlation coefficient, s standard deviation, π' transmissive factors.

Parameter	Series			
	Ia	IIa	Ib	IIb
n	9	8	7	8
$\varrho_{\pi,R}$	0.179 ± 0.005	0.073 ± 0.004	0.153 ± 0.004	0.057 ± 0.007
$-E_{1/2}^0$	1.420 ± 0.002	0.553 ± 0.001	1.351 ± 0.001	0.511 ± 0.000
r	0.997	0.988	0.987	0.954
s	0.003	0.003	0.006	0.005
π'	0.61 ± 0.05	0.68 ± 0.05	0.53 ± 0.06	0.55 ± 0.07

zation energy of the system should be partially linear[4]. It can be also stated that the increase of the conjugation between the transfer and reaction centres results in inhibition of the transfer of the electron effects of the substituents to the reaction centre, which follows from the π' value for the benzene ring $(0.27 \pm 0.03$ (ref.[16]) and 0.32 (ref.[17])) which are minimal compared with the studied heterocycles. The ability of the studied systems to transfer the effects of substituents then decreases in the order furan > thiophene > benzene, *i.e.* in the order in which the values of the delocalization energies increase in these systems.

It can be concluded that the determined value of the ratio $\varrho_{Thio}/\varrho_{Fu} = 0.83$ is in very good agreement with the values of other systems containing oxygen and sulphur bridges[13] (0.86 and 0.89). Further it was verified that, with decreasing pH in series I, the values of the $\varrho_{\pi,R}$ constants also decrease, as has been found with similar systems[1]. Furthermore, at pH ~2.5, where the corresponding aldehydes yield one one-electron wave, the values of the correlation coefficients are on the border of statistical validity, which results in a substantial increase in the errors of the values of the transmissive factors.

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