

## TRANSMISSION OF SUBSTITUENT EFFECT ACROSS THE FURAN RING

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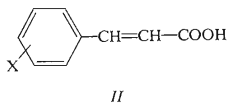
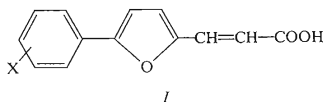
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Half-wave potential values, apparent dissociation constants and wavenumbers of IR spectral bands of substituted 3-(5-phenyl-2-furyl)acrylic and 3-arylacrylic acids were correlated with  $\sigma$  substituent constants. The transmission coefficients across the furan ring,  $\pi'$ , were calculated from the obtained reaction constants  $\rho$  and compared with the values of  $\pi'$  found for other systems.

The coefficients of transmission across the furan ring,  $\pi'$ , were hitherto studied<sup>1-6</sup> and calculated mainly on the basis of the infrared spectra. In order to determine the values of  $\pi'$  also by other methods and to compare the results obtained by various approaches, we investigated 3-(5-aryl-2-furyl)acrylic acids *I*. These compounds contain several reactive centers (CH=CH, C=O, —OH) and therefore they are suitable not only for spectral but also for potentiometric and polarographic studies. The parameters of linear correlations for a given series can be thus calculated from a greater number of independent experimental values.

Substituted 3-phenylacrylic acids *II* were used as model compounds. From the method of preparation of the derivatives *I* and *II* we can assume that the double bond in all the studied derivatives has *trans*-configuration. The polarographic study of compounds *I* was based on results of previous studies<sup>7,8</sup> in which 3-phenylacrylic acid and its analogues were reduced in aqueous-ethanolic solutions of Li<sub>2</sub>SO<sub>4</sub> (ref.<sup>7</sup>) and in tetramethylammonium hydroxide<sup>8</sup>. In these media the multiple bond in the studied systems is reduced with two electrons in one step to give corresponding saturated derivatives.

Polarographic study of the compounds *I* and *II* has shown that the relationships  $i = f(c, h^{1/2})$  are linear and pass through the origin indicating thus a diffusion character of the processes on the Hg-electrode. The  $E_{1/2}$  values are affected by substituents and they are 40–80 mV more positive for the compounds *I* as compared with the values found for the compounds *II*. All the derivatives show in the supporting electrolyte (0.1M-LiCl) a well-developed cathodic wave of the value  $n \cdot \alpha$  in the interval 0.9–1.1.



The  $pK_a$  values were determined from half-neutralisation points on the titration curves. The dissociation constants were calculated also numerically from the experimental values, using the relationship for a monobasic acid<sup>9</sup>

$$pK_a = pH + \log (c_{HA}/c_{A^-}),$$

where  $c_{HA}$  and  $c_{A^-}$  is the stoichiometric concentration of non-dissociated and dissociated acid, respectively. The measured values of  $\nu(C=O)$  were also used for the calculation of the coefficients  $\pi'$ .

TABLE I  
Basic Polarographic Characteristics, Values of  $pK_a$  and Wavenumbers of Carbonyl Bands for the Series *I* and *II*, and the Corresponding Substituent Constants

No	X	$-E_{1/2}, V$	$i/c$	$pK_a$		$\nu(CO), cm^{-1}$	$\sigma$
				num.	graph.		
3-(5-Aryl-2-furyl)acrylic acids <i>I</i>							
1	4-OCH <sub>3</sub>	1.455	2.1	6.92	—	1 689	-0.27
2	4-CH <sub>3</sub>	1.442	2.2	6.80	—	1 690	-0.17
3	H	1.429	1.8	6.67	—	1 691	0.00
4	4-Cl	1.408	2.4	6.62	—	1 698	0.23
5	4-Br	1.412	1.5	6.63	—	1 695	0.23
6	3-Cl	1.402	2.0	6.50	—	1 698	0.37
7	3-CF <sub>3</sub>	1.387	2.2	6.46	—	—	0.43
8	3-CF <sub>3</sub> , 4-Cl	1.373	1.8	6.52	—	—	0.66
9	4-NO <sub>2</sub>	—	—	6.37	—	1 703	0.78
3-Arylacrylic acids <i>II</i>							
1	4-CH <sub>3</sub>	1.520	2.7	5.62	5.58	1 688	-0.17
2	3,4-(OCH <sub>3</sub> ) <sub>2</sub>	1.512	2.5	5.68	5.62	1 678	-0.14
3	H	1.501	2.9	5.45	5.48	1 692	0.00
4	3-OCH <sub>3</sub>	1.480	2.9	5.42	5.40	1 695	0.12
5	4-Cl	1.472	2.9	5.38	5.36	1 699	0.23
6	3-F	1.454	2.7	5.23	5.22	1 700	0.34
7	3-Cl	1.446	2.7	5.19	5.18	1 702	0.37
8	3,4-Cl <sub>2</sub>	1.417	2.7	5.07	5.10	1 706	0.60

The polarographic characteristics, apparent  $pK_a$  values and wavenumbers of the C=O bands for the investigated compounds are summarised in Table I, together with the corresponding values of substituent constants,  $\sigma$ . The  $pK_a$  values for the compounds *I* are taken from ref.<sup>10</sup>. The half-wave potentials, dissociation constants and wavenumbers were plotted against  $\sigma$  substituent constants<sup>11</sup> affording good linear relationships for both series of compounds (Table II). Comparison of the reaction constants  $\rho$  obtained for the series *I* with those obtained for the series *II* shows a somewhat smaller influence of substituents on the reaction center in the furan derivatives. The values of the transmission coefficients across the furan ring in compounds *I*,  $\pi'$ , were calculated from the relationship  $\pi' = \rho/\rho_0$ , where  $\rho$  and  $\rho_0$  are the reaction constants (slopes) for the series *I* and *II*, respectively. The extent of the damping effect of the furan ring is seen from Table III.

There is a good agreement between the results obtained by different methods (polarography, potentiometry and IR spectroscopy). The results of the present study

TABLE II  
Statistical Parameters of Linear Relationships for Studied Series *I* and *II*

Parameter <sup>a</sup>	<i>n</i>	$\rho \pm s_\rho$	$q \pm s_q$	<i>r</i>	<i>s</i>
Series <i>I</i>					
$E_{1/2}$	8	0.087 $\pm$ 0.004	-1,429 $\pm$ 0.002	0.994	0.003
$pK_a$	9	0.458 $\pm$ 0.060	6.725 $\pm$ 0.045	0.945	0.060
$\nu(\text{CO})$	7	14.098 $\pm$ 1.483	1 692.5 $\pm$ 0.655	0.973	1.290
Series <i>II</i>					
$E_{1/2}$	8	0.132 $\pm$ 0.004	-1.497 $\pm$ 0.002	0.996	0.003
$pK_a$	8	0.769 $\pm$ 0.063	5.505 $\pm$ 0.030	0.980	0.045
$\nu(\text{CO})$	8	25.178 $\pm$ 1.370	1 691.0 $\pm$ 0.650	0.990	0.970

<sup>a</sup> *n* Number of derivatives in the series,  $\rho$  slope and its error,  $q$  intercept and its error, *r* correlation coefficient, *s* standard deviation.

TABLE III  
Values of Transmission Coefficients across the Furan Ring

Transmission coefficient $\pi'$	0.66	0.59	0.56
Measured quantity	$E_{1/2}$	$pK_a$	$\nu(\text{C=O})$

also agree with the values obtained previously<sup>1-6</sup>. Although the mean determined values of the transmission coefficients are higher than the calculated ones, they correspond to the assumption that the dependence of  $\pi'$  on the delocalisation energy of the system will have a partly linear character<sup>3</sup>.

## EXPERIMENTAL

### Materials and Equipment

The investigated substituted 3-(5-phenyl-2-furyl)acrylic<sup>10</sup> and 3-arylacrylic<sup>12</sup> acids were prepared by Perkin synthesis. The IR absorption spectra were taken by a UR 20 (Zeiss, Jena) spectrophotometer, calibrated with a polystyrene foil. The acids were titrated on a Titrator TT (Radiometer, Copenhagen) using a glass G 202B electrode and a calomel K 401 electrode; accuracy  $\pm 0.02$  pH units. The mercury dropping electrode had dropping time  $t_1$  2.8 s (reservoir height  $h$  60 cm,  $m$  2.3 mg s<sup>-1</sup>). The values of  $E_{1/2}$  were measured against a non-polarised saturated calomel electrode (system of three electrodes), using a QTK-compensator (Metra, Blansko), accuracy  $\pm 0.2$  mV. Constant temperature was kept by an ultrathermostat Wobster U8 (Prüfgeräte, Mädingen—Dresden). The parameters of the linear correlations were calculated using the statistical relationships<sup>13</sup> (Hewlett-Packard calculator 9100 B).

### Methods

The polarographic measurements were performed in aqueous-ethanolic solutions at 20°C, supporting electrolyte 0.1M-LiCl, depolarisator concentration 0.25 mM. Values of the apparent dissociation constants,  $pK_a$ , were determined by potentiometric titration of aqueous-ethanolic (20 ml, 0.005M) solutions of the corresponding acids with 0.1M-NaOH at 25°C. All polarographic and potentiometric measurements were carried out under nitrogen; concentration of ethanol 50%. IR spectra were taken in 0.01M chloroform solutions.

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