

INFRARED SPECTRA OF SUBSTITUTED 2-BENZYLIDENE-,  
2-(5-PHENYL-2-THENYLIDENE)-, AND 2-(5-PHENYL-2-FURFURYLIDENE)-  
4,7-DITHIA-4,5,6,7-TETRAHYDRO-1,3-INDANDIONES, TRANSMISSION  
OF SUBSTITUENT EFFECTS BY THE THIOPHENE AND FURAN RINGS

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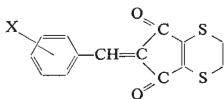
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Dedicated to Professor S. Stankovianský on the occasion of his 65th birthday.

Infrared spectra of 37 substituted 2-benzylidene-, 2-(5-phenyl-2-thenylidene)-, and 2-(5-phenyl-2-furfurylidene)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones were studied in tetrachloromethane and chloroform solutions in the region of stretching vibrations of carbonyl groups. In all the three compound series the statistical analysis of linear correlations between the frequencies of the C=O stretching vibrations and the substituent constants was performed. The transmissive factors for the thiophene and furan rings in tetrachloromethane as well as in chloroform were calculated from the slopes of the statistically most significant linear correlations (*i.e.* from those of the correlations between the arithmetic mean of the frequencies of the symmetric and asymmetric C=O vibration and the  $\sigma^+$  constants). In tetrachloromethane, the substituent effects were found to be transmitted by the thiophene ring to a less extent than by the furan ring. The solvent effect on the transmission by the thiophene ring is discussed in comparison with that effect on the transmission by the furan ring.

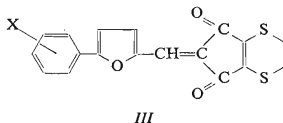
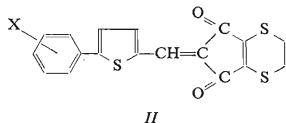
In the previous papers<sup>1,2</sup> we have studied the infrared spectra of substituted 2-(5-phenyl-2-furfurylidene)-1,3-indandiones and 5-phenyl-2-furaldehydes in comparison with the spectra of substituted 2-benzylidene-1,3-indandiones and benzaldehydes. In those series we utilized the linear correlations found between the frequencies of the C=O stretching vibration and the substituent constants for the calculation of the transmissive factors of substituent effects by the furan ring.

In the paper presented we are concerned with the quantitative study of the transmission of substituent effects by the thiophene ring in comparison with the transmission by the furan ring. For this purpose we use the linear correlations between



I

the frequencies of the C=O stretching vibration and the substituent constants in the series of substituted 2-benzylidene-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones (*I*), 2-(5-phenyl-2-thenylidene)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones (*II*), and 2-(5-phenyl-2-furfurylidene)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones (*III*).



## EXPERIMENTAL

The studied compounds of the types *I–III* except the amino and hydroxy derivatives were prepared by means of condensation of 4, 7-dithia-4,5,6,7-tetrahydro-1,3-indandione with substituted benzaldehydes, 5-phenyl-2-thiophenecarboxaldehydes, and 5-phenyl-2-furaldehydes in 96% ethanol under the catalytic effect of piperidine. The amino derivatives were obtained by the reduction of the corresponding nitro derivatives with tin dichloride in the medium of acetic acid. The hydroxy derivatives were prepared by the Zeisel reaction from the corresponding methoxy derivatives. The compounds studied were purified before the spectral measurements by repeated crystallization from acetic acid, except the amino derivatives, which were crystallized from acetone. A detailed description of the synthesis of the compounds of the types *I–III* together with their analytical data and physical constants is to be published in the paper<sup>3</sup>. Infrared spectra of compounds *I–III* were measured in the region of 1800–1600  $\text{cm}^{-1}$  on a Zeiss UR 20 spectrophotometer. The wavenumber scale of the instrument was calibrated using the standard spectrum of the indene-camphor-cyclohexanone mixture<sup>4</sup>. The accuracy of the frequency reading was  $\pm 0.5 \text{ cm}^{-1}$ . Solutions of the compounds in tetrachloromethane and cell thicknesses of 0.1, 0.25, 0.5, and 1 cm were used for the measurements. The solution concentrations were chosen to keep the maximum absorption at 70–75%. The  $\sigma$  constants published by McDaniel and Brown<sup>5</sup> and the  $\sigma^+$  constants according to Brown and Okamoto<sup>6</sup> were used for the Hammett correlations. The parameters of linear correlations were calculated by means of the digital computer Regnezentralen Gier using nonapproximated statistical relations<sup>7</sup>.

## RESULTS AND DISCUSSION

In the spectra of all the derivatives of 4,7-dithia-4,5,6,7-tetrahydro-1,3-indandione (*I–III*) studied, a doubled absorption band is observed in the region of the C=O stretching vibrations. Analogously to the case of other derivatives of 1,3-indandione<sup>8</sup>, the less intense high-frequency band and the more intense low-frequency band can be attributed to the symmetric ( $\nu_s$ ) and asymmetric ( $\nu_{as}$ ) C=O stretching vibrations, resp., of the cyclic 1,3-dicarbonyl system. The frequencies  $\nu_s$  and  $\nu_{as}$ , as well as their arithmetic means for the compound series *I–III* are given in Tables I–III. The frequencies of the symmetric as well as asymmetric vibrations of the compounds of type *I*, *II*, and *III* are 5–17, 2–12, and 5–13  $\text{cm}^{-1}$ , resp., lower than those of the corresponding 2-benzylidene-1,3-indandiones<sup>9</sup>, 2-(5-phenyl-2-thenylidene)-1,3-indandiones<sup>10</sup>, and 2-(5-phenyl-2-furfurylidene)-1,3-indandiones<sup>1</sup>, resp. This frequency decrease can be explained by the electron-donor effect of the sulfur atoms on the carbonyl groups, similarly to the case of 3-phenyl-

methylene-4,7-dithia-4,5,6,7-tetrahydrophthalides<sup>11</sup>. Passing from tetrachloromethane to chloroform, the frequencies of the symmetric as well as asymmetric C=O vibrations of the compounds *I–III* exhibit a 2–9 cm<sup>-1</sup> decrease. The frequencies of the C=O stretching vibration of the compounds *II* and *III* are always lower than those of the compounds *I*, which is due to the electron-donor effect of the oxygen or sulfur heteroatom, as well as to the lengthening of the conjugated system.

Similarly to the series of substituted 2-arylidene-1,3-indandiones<sup>1,10</sup>, the Hammett correlations between the frequencies of the C=O stretching vibration and the substituent constants are valid also in the case of their 4,7-dithia-4,5,6,7-tetrahydro analogs (*I–III*). In all the compound series studied, the statistical analyses of the Hammett correlations of the types  $\bar{\nu}$  vs  $\sigma$ ,  $\bar{\nu}$  vs  $\sigma^+$ ,  $\nu_{as}$  vs  $\sigma$ ,  $\nu_s$  vs  $\sigma$ ,  $\nu_{as}$  vs  $\sigma^+$ , and  $\nu_s$  vs  $\sigma^+$  were carried out for data obtained in chloroform and tetrachloromethane. The linear relations of the type  $\bar{\nu}$  vs  $\sigma^+$  were found to be statistically the most important in most cases, which is in a good agreement with the results of our previous papers<sup>1,10</sup>. The arithmetic means of the correlation coefficients for the couples

TABLE I

The C=O Stretching Frequencies (cm<sup>-1</sup>) and the Corresponding  $\sigma$  and  $\sigma^+$  Substituent Constants for Substituted 2-Benzylidene-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones (*I*)

X	CCl <sub>4</sub>			CHCl <sub>3</sub>			$\sigma$	$\sigma^+$
	$\nu_s$	$\nu_{as}$	$\bar{\nu}$	$\nu_s$	$\nu_{as}$	$\bar{\nu}$		
4-N-(CH <sub>3</sub> ) <sub>2</sub>	1 717	1 671	1 694·0	1 712	1 664	1 688·0	-0·83	-1·70
4-NH <sub>2</sub>	— <sup>a</sup>	— <sup>a</sup>	—	1 715	1 669	1 692·0	-0·66	-1·30
4-OH	1 721	1 677	1 690·0	1 717	1 671	1 694·0	-0·37	-0·92
4-OH-3-OCH <sub>3</sub> <sup>b</sup>	1 723	1 675	1 699·0	1 717	1 669	1 693·0	-0·25	-0·87
4-OCH <sub>3</sub>	1 722	1 678	1 700·0	1 717	1 671	1 694·0	-0·27	-0·78
4-CH <sub>3</sub>	1 722	1 680	1 701·0	1 720	1 674	1 697·0	-0·17	-0·31
H	1 724	1 681	1 702·5	1 722	1 676	1 699·0	0·00	0·00
3-OCH <sub>3</sub>	1 724	1 680	1 702·0	1 723	1 676	1 699·5	0·12	0·05
4-I	1 724	1 682	1 703·0	1 723	1 677	1 700·0	0·18	0·05
4-Cl	1 722	1 679	1 700·5	1 722	1 677	1 699·5	0·23	0·11
3-I	1 726	1 682	1 704·0	1 723	1 677	1 700·0	0·35	0·36
3-Cl	1 726	1 681	1 703·5	1 723	1 677	1 700·0	0·37	0·40
4-Br	1 726	1 682	1 704·0	1 723	1 678	1 700·5	0·39	0·40
4-CN	1 727	1 683	1 705·0	1 724	1 679	1 701·5	0·66	0·66
3-NO <sub>2</sub>	— <sup>a</sup>	— <sup>a</sup>	—	1 724	1 679	1 701·5	0·71	0·67
4-NO <sub>2</sub>	— <sup>a</sup>	— <sup>a</sup>	—	1 724	1 680	1 702·0	0·78	0·79

<sup>a</sup> Spectra were not measured because of the low solubility of the compounds in tetrachloromethane. <sup>b</sup> Listed in this Table for simplification, although the formula *I* is not valid for this compound; the  $\sigma$  and  $\sigma^+$  constant calculated as the sum of  $\sigma$  resp.  $\sigma^+$  for the substituents 4-OH and 3-OCH<sub>3</sub>.

TABLE II

The C=O Stretching Frequencies ( $\text{cm}^{-1}$ ) for Substituted 2-(5-Phenyl-2-thenylidene)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones (II)

$X^a$	$\text{CCl}_4$			$\text{CHCl}_3$		
	$\nu_s$	$\nu_{as}$	$\bar{\nu}$	$\nu_s$	$\nu_{as}$	$\bar{\nu}$
4-NH <sub>2</sub>	1 723	1 677	1 700.0	1 718	1 668	1 693.0
4-OCH <sub>3</sub>	1 723	1 679	1 701.0	1 718	1 670	1 694.0
4-CH <sub>3</sub>	1 725	1 678	1 701.5	1 719	1 670	1 694.5
3-CH <sub>3</sub>	1 725	1 679	1 702.0	1 719	1 671	1 695.0
H	1 725	1 679	1 702.0	1 719	1 671	1 695.0
4-Cl	1 725	1 680	1 702.5	1 720	1 672	1 696.0
4-Br	1 726	1 680	1 703.0	1 720	1 672	1 696.0
3-Br	1 726	1 680	1 703.0	1 720	1 671	1 695.5
4-NO <sub>2</sub>	1 726	1 682	1 704.0	1 721	1 674	1 697.5

<sup>a</sup> For 3-CH<sub>3</sub>,  $\sigma = -0.07$  and  $\sigma^+ = -0.07$ ; for 4-Br,  $\sigma = 0.23$  and  $\sigma^+ = 0.15$ . For the other substituents, see Table I for the  $\sigma$  and  $\sigma^+$  values.

TABLE III

The C=O Stretching Frequencies ( $\text{cm}^{-1}$ ) for Substituted 2-(5-Phenyl-2-furfurylidene)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones (III)

$X^a$	$\text{CCl}_4$			$\text{CHCl}_3$		
	$\nu_s$	$\nu_{as}$	$\bar{\nu}$	$\nu_s$	$\nu_{as}$	$\bar{\nu}$
4-OH	1 721	1 675	1 698.0	1 715	1 668	1 691.5
4-OCH <sub>3</sub>	1 722	1 676	1 699.0	1 715	1 669	1 692.0
4-CH <sub>3</sub>	1 724	1 677	1 700.5	1 715	1 670	1 692.5
3-NH <sub>2</sub>	1 724	1 676	1 700.0	1 717	1 670	1 693.5
H	1 724	1 677	1 700.5	1 716	1 670	1 693.0
4-Cl	1 724	1 677	1 700.5	1 717	1 671	1 694.0
4-Br	1 724	1 678	1 701.0	1 716	1 670	1 693.0
3-F	— <sup>b</sup>	— <sup>b</sup>	—	1 715	1 671	1 693.0
3-Cl	1 725	1 678	1 701.5	1 717	1 671	1 694.0
3-Br	1 725	1 679	1 702.0	1 717	1 671	1 694.0
3-NO <sub>2</sub>	— <sup>b</sup>	— <sup>b</sup>	—	1 718	1 673	1 695.5
4-NO <sub>2</sub>	— <sup>b</sup>	— <sup>b</sup>	—	1 719	1 674	1 696.5

<sup>a</sup> For 3-NH<sub>2</sub>,  $\sigma = -0.16$  and  $\sigma^+ = -0.16$ ; for 3-F,  $\sigma = 0.34$  and  $\sigma^+ = 0.35$ . For the other substituents, see Table I and II for the  $\sigma$  and  $\sigma^+$  values. <sup>b</sup> Spectrum was not measured because of the low solubility of the compounds in tetrachloromethane.

of series *I* and *III* have in most cases also the highest values for the correlations of the  $\bar{\nu}$  vs  $\sigma^+$  type. For that reason, similarly to the papers<sup>1,10</sup>, the slopes of those selected correlations (Table IV) were used for the calculation of the transmissive factors of substituent effects by the thiophene and furan rings according to the relations

$$\pi'(\text{Thi}) = \varrho_{\text{II}}/\varrho_{\text{I}}$$

$$\pi'(\text{Fu}) = \varrho_{\text{III}}/\varrho_{\text{I}}$$

where  $\pi'(\text{Thi})$  and  $\pi'(\text{Fu})$  are the transmissive factors for the thiophene ring (more exactly for the 2,5-thienylene bridge) and for the furan ring (*i.e.* for the 2,5-furylene bridge), resp.;  $\varrho_{\text{I}}$ ,  $\varrho_{\text{II}}$ , and  $\varrho_{\text{III}}$  are the slopes of the linear correlations of the  $\bar{\nu}$  vs  $\sigma^+$  type for the compound series *I*, *II*, and *III*, resp. The values of transmissive factors calculated in that way are  $\pi'(\text{Thi}) = 0.45 \pm 0.07$  and  $0.37 \pm 0.06$  in tetrachloromethane and chloroform, resp., and  $\pi'(\text{Fu}) = 0.60 \pm 0.12$  and  $0.43 \pm 0.03$  in the two solvents, resp. The values  $\pi'(\text{Fu})$  in the two solvents are in a good agreement with those published in the papers<sup>1,2</sup>.

When comparing the  $\pi'(\text{Thi})$  values calculated from the data measured in tetrachloromethane and chloroform one finds the solvent effect on the transmission by the thiophene ring to be practically negligible. On the other hand, from the comparison of the  $\pi'(\text{Fu})$  values in the two solvents it can be concluded that the substituent effects are transmitted by the furan ring in chloroform to a less extent than in tetrachloromethane. The reason of this was explained in paper<sup>1</sup> by the hydrogen bonding between the oxygen atom of the furan ring and chloroform molecules. The negligible solvent

TABLE IV

Statistical Parameters of Selected Hammett Correlations of the  $\bar{\nu}$  vs  $\sigma^+$  Type for the Compound Series *I—III*

Series	Solvent	<i>n</i>	<i>r</i>	$\varrho$	$s_{\varrho}$	<i>q</i>	$s_q$	<i>s</i>	$\bar{r}$
<i>I</i>	CHCl <sub>3</sub>	16	0.986	5.40	0.25	1 698.4	0.1	0.72	—
<i>I</i>	CCl <sub>4</sub>	13	0.959	4.14	0.37	1 702.2	0.3	0.88	—
<i>II</i>	CHCl <sub>3</sub>	9	0.948	1.98	0.25	1 695.4	0.1	0.44	0.967
<i>II</i>	CCl <sub>4</sub>	9	0.981	1.88	0.14	1 702.3	0.0	0.25	0.970
<i>III</i>	CHCl <sub>3</sub>	12	0.880	2.34	0.40	1 693.4	0.1	0.70	0.933
<i>III</i>	CCl <sub>4</sub>	9	0.957	2.48	0.28	1 700.6	0.1	0.58	0.933

*n* Number of compounds used in the correlation; *r* correlation coefficient;  $\varrho$  slope;  $s_{\varrho}$  error of the slope; *q* intercept;  $s_q$  error of the intercept; *s* standard deviation;  $\bar{r}$  arithmetic mean of the correlation coefficients for the compound series *I* and *II*, resp. *I* and *III*.

effect in the case of the transmission by the thiophene ring can be attributed to the lower ability of the sulfur atom in the thiophene ring to form hydrogen bonds.

Finally, from the comparison of the  $\pi'$ (Fu) and  $\pi'$ (Thi) values in tetrachloromethane (*i.e.* in a medium practically not interacting with the transmissive center) it follows that the substituent effects are transmitted by the furan ring more readily than by the thiophene ring.

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