

## INFLUENCE OF SOLVENTS ON TRANSMISSION OF SUBSTITUENT EFFECTS BY THE OXYGEN AND SULFUR BRIDGES

A. PERJÉSSY<sup>a</sup>, G. MELIKIAN<sup>b</sup>, P. HRNČIAR<sup>a</sup> and M. LÁCOVÁ<sup>a</sup>

<sup>a</sup> Department of Organic Chemistry,  
Comenius University, 801 00 Bratislava,

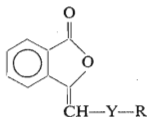
<sup>b</sup> Department of Organic Chemistry,  
Jerevan State University, Jerevan, Armenia, U.S.S.R.

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Carbonyl stretching frequencies measured in tetrachloromethane for a series of 3-arylmethylenephthalides, 3-aryloxymethylenephthalides, and 3-arylthiomethylenephthalides were correlated with the Hammett  $\sigma$  substituent constants. In linear correlations, the  $\sigma_p$  constants were successfully used in the case of *ortho*-substituted derivatives. For 4-substituted 1-naphthyl groups, the new  $\sigma_{Ar}$  constants were calculated. Slopes of linear correlations were used in calculations of transmissive factors for the —O— and —S— bridges in tetrachloromethane. As inferred from comparison of transmissive factors in tetrachloromethane and chloroform, the ability of the —O— bridge to transmit the substituent effect in chloroform is lowered by the formation of hydrogen bondings between the transmission center and the solvent molecules. In the case of the —S— bridge, the influence of the solvent on transmission of substituent effects is negligible. The experimental values of transmissive factors for the —O— and —S— bridges may be used as partial data in calculations of transmissive factors for more complex systems.

In preceding work<sup>1-3</sup>, we have investigated carbonyl stretching frequencies in chloroform of a series of 3- and 4-substituted *trans*-3-phenylmethylenephthalides, *trans*-3-phenyloxymethylenephthalides, *trans*-3-phenylthiomethylenephthalides and of a series of 4-substituted *trans*-3-(1-naphthylmethylene)phthalides. Using slopes of  $\nu(\text{C}=\text{O})$  vs  $\sigma$  linear relationships, transmissive factors for the —O— and —S— bridges in chloroform were determined. As shown by investigations<sup>4-8</sup> on transmission of substituent effects by the furan and thiophene rings in chloroform as well as in tetrachloromethane, the transmission by the furan ring is highly dependent on the solvent.

In the present work, we have determined transmissive factors for the —O— and —S— bridges in tetrachloromethane, *i.e.*, an aprotic, nonpolar solvent, and have investigated the influence of the solvent on transmission of substituent effects by



*I*, Y = —; *II*, Y = O; *III*, Y = S; for R see Table I and II

these bridges. The carbonyl stretching frequencies have been measured in tetrachloromethane for a series of thirty *trans*-3-arylmethylenephthalides *I*, eleven *trans*-3-aryloxymethylenephthalides *II*, and nine *trans*-3-arylthiomethylenephthalides *III*, and correlated with the Hammett  $\sigma$  substituent constants.

## EXPERIMENTAL

For the preparation and purification of compounds *I*–*III* see the earlier papers<sup>9–12</sup>. The carbonyl stretching frequencies were measured in tetrachloromethane on a Zeiss UR 20 spectrophotometer by the earlier reported technique<sup>4–8</sup>. The linear  $\nu(\text{C}=\text{O})$  vs  $\sigma$  correlations were processed by means of statistic relations<sup>13</sup> on a Hewlet Packard 9100 B computer (standard program).

## RESULTS AND DISCUSSIONS

The carbonyl stretching frequencies in tetrachloromethane of the compound series *I*–*III* are shown in Tables I and II. In all the three series there exist fair linear correlations between the carbonyl stretching frequencies and the Hammett  $\sigma$  constants<sup>14</sup> (Fig. 1). Statistic evaluation of these correlations is shown in Table III along with regressive parameters of analogous correlations of the compound series *I*–*III* obtained<sup>1,2</sup> by measurements in chloroform.

As it may be seen from Fig. 1, the series of compounds *I* and *II* also comprise the carbonyl stretching frequencies of compounds containing *ortho*-substituents on the

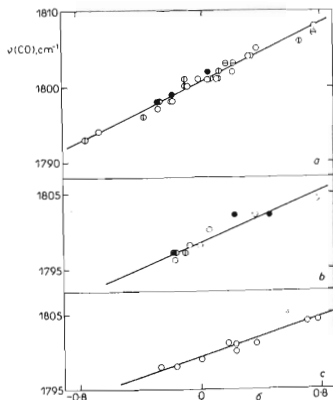


FIG. 1

Linear Correlations of the  $\nu(\text{C}=\text{O})$  vs  $\sigma$ . Type in Tetrachloromethane (in  $\text{cm}^{-1}$ ) for *a* 3-Arylmethylenephthalides *I*, *b* 3-Aryloxymethylenephthalides *II*, and *c* 3-Arylthiomethylenephthalides *III*

R =  $\text{C}_6\text{H}_5$ , 3- $\text{XC}_6\text{H}_4$ , and 4- $\text{XC}_6\text{H}_4$  (○); 2- $\text{XC}_6\text{H}_4$  (●); 1- $\text{C}_{10}\text{H}_7$ , 2- $\text{C}_{10}\text{H}_7$ , and 4-X-1- $\text{C}_{10}\text{H}_6$  (⊙); 4-X- $\text{C}_6\text{H}_4 \equiv$  2-X- $\text{C}_6\text{H}_4$  (⊖).

benzene ring (compounds 15–20 and 37–39). In this case, the corresponding  $\sigma_p$  substituent constants were used in linear correlations. Such a use of  $\sigma_p$  constants in the case of *ortho*-substituents is according to Charton<sup>15</sup> justified when the substituent is distant enough from the reaction center. The  $\sigma_p^+$  constants were successfully used for the *ortho*-substituted chalcones in linear  $\nu(\text{C}=\text{O})$  vs  $\sigma^+$  correlations by Boykin and coworkers<sup>16</sup>. In the present case, *i.e.*, in series of compounds *I* and *II*, the substituent is distant enough from the carbonyl group and consequently, the use of  $\sigma_p$  constants in the case of *ortho*-substituents fairly complies with the linear  $\nu(\text{C}=\text{O})$  vs  $\sigma$  correlations.

In the earlier papers<sup>1,3</sup>, we have determined the  $\sigma_{Ar}$  ( $\sigma_a$ ) constants for the 1-naphthyl and 2-naphthyl group. The use of these constants in the compound series *I* and *II* satisfactorily complies with the linear  $\nu(\text{C}=\text{O})$  vs  $\sigma$  correlations. It has been earlier observed<sup>3</sup> that the slopes of the

TABLE I

Carbonyl Stretching Frequencies (in  $\text{cm}^{-1}$ ) of *trans*-3-Phenyl- and *trans*-3-Naphthylmethylene-phthalides in Tetrachloromethane and the Corresponding  $\sigma$  Substituent Constants

Compound	X <sup>a</sup>	$\nu(\text{C}=\text{O})$	$\sigma^b$	Compound	X <sup>a</sup>	$\nu(\text{C}=\text{O})$	$\sigma^b$
<i>Phenyl derivatives</i>				<i>Phenyl derivatives</i>			
1	4-NH <sub>2</sub>	1 794	-0.66	18	2-I	1 804	0.18 <sup>c</sup>
2	4-OCH <sub>3</sub>	1 797	-0.27	19	2-Cl	1 803	0.23 <sup>c</sup>
3	4-CH <sub>3</sub>	1 798	-0.17	20	2-NO <sub>2</sub>	1 807	0.78 <sup>c</sup>
4	3-CH <sub>3</sub>	1 800	-0.07	<i>1-Naphthyl derivatives</i>			
5	H	1 801	0.00	21	4-NH <sub>2</sub>	1 793	-0.75 <sup>d</sup>
6	4-F	1 801	0.06	22	4-OCH <sub>3</sub>	1 796	-0.36 <sup>d</sup>
7	3-OCH <sub>3</sub>	1 801	0.12	23	4-CH <sub>3</sub>	1 798	-0.26 <sup>d</sup>
8	4-I	1 803	0.18	24	4-NHCOCH <sub>3</sub>	1 801	-0.09 <sup>d</sup>
9	4-Cl	1 802	0.23	25	H	1 800	-0.09 <sup>e</sup>
10	4-Br	1 803	0.23	26	4-I	1 801	0.09 <sup>d</sup>
11	3-F	1 804	0.34	27	4-Cl	1 802	0.14 <sup>d</sup>
12	3-I	1 804	0.35	28	4-Br	1 801	0.14 <sup>d</sup>
13	3-Br	1 805	0.39	29	4-NO <sub>2</sub>	1 806	0.69 <sup>d</sup>
14	4-NO <sub>2</sub>	1 808	0.78	30	H <sup>f</sup>	1 798	-0.165 <sup>e</sup>
15	2-OCH <sub>3</sub>	1 798	-0.27 <sup>c</sup>				
16	2-CH <sub>3</sub>	1 799	-0.17 <sup>c</sup>				
17	2-F	1 802	0.06 <sup>c</sup>				

<sup>a</sup> X designates the substituent on the aromatic ring of the group R (see Formula I). <sup>b</sup> Data taken from ref.<sup>14</sup> <sup>c</sup> In the case of the 2-substituents, the  $\sigma$  constants<sup>14</sup> of the corresponding substituents at position 4 were taken. <sup>d</sup> Calculated according to the equation (1). <sup>e</sup> Data taken from ref.<sup>3</sup> as average values. <sup>f</sup> 2-Naphthyl derivative.

TABLE II

Carbonyl Stretching Frequencies (in  $\text{cm}^{-1}$ ) of *trans*-3-Phenyloxymethylenephthalides *II* and *trans*-3-Phenylthiomethylenephthalides *III* in Tetrachloromethane and the Corresponding  $\sigma$  Substituent Constants

Compound	X <sup>a</sup>	$\nu(\text{C}=\text{O})$	$\sigma^b$	Compound	X <sup>a</sup>	$\nu(\text{C}=\text{O})$	$\sigma^b$
<i>Series II</i>				<i>Series III</i>			
31	4-CH <sub>3</sub>	1 796	-0.17	42	4-OCH <sub>3</sub>	1 798	-0.27
32	3-C <sub>2</sub> H <sub>5</sub>	1 798	-0.07	43	4-CH <sub>3</sub>	1 798	-0.17
33	H	1 798	0.00	44	H	1 799	0.00
34	4-F	1 800	0.06	45	4-I	1 801	0.18
35	3-Cl	1 802	0.37	46	4-Cl	1 800	0.23
36	4-NO <sub>2</sub>	1 804	0.78	47	4-Br	1 801	0.23
37	2-CH <sub>3</sub>	1 797	-0.17 <sup>c</sup>	48	3-Cl	1 801	0.37
38	2-Cl	1 802	0.23 <sup>c</sup>	49	3-NO <sub>2</sub>	1 804	0.71
39	2,4-Cl <sub>2</sub>	1 802	0.46 <sup>c</sup>	50	4-NO <sub>2</sub>	1 804	0.78
40	H <sup>d</sup>	1 797	-0.09 <sup>e</sup>				
41	H <sup>f</sup>	1 797	-0.165 <sup>e</sup>				

<sup>a</sup> X designates the substituent on the aromatic ring of the group R (see Formulae *II* and *III*).

<sup>b</sup> Data taken from ref. <sup>14</sup>. <sup>c</sup> In the case of the 2-substituents, the  $\sigma$  constants<sup>14</sup> of the corresponding substituents at position 4 were taken. <sup>d</sup> R = 1-Naphthyl. <sup>e</sup> Data taken from ref. <sup>3</sup> as average values. <sup>f</sup> R = 2-Naphthyl.

TABLE III

Statistic Parameters of the Linear  $\nu(\text{C}=\text{O})$  vs  $\sigma$  Correlations for the Series of Compounds *I-III*  
*n*, Number of compounds in the correlation; *r*, correlation coefficient; *q*, slope; *q*, intercept; *s*, standard deviation.

Series	Solvent	<i>n</i>	<i>r</i>	<i>q</i>	<i>q</i>	<i>s</i>
<i>I</i>	CCl <sub>4</sub>	30	0.979	9.67	1 800.5	0.83
<i>I</i> <sup>a</sup>	CHCl <sub>3</sub>	12	0.985	12.02	1 782.2	0.80
<i>II</i>	CCl <sub>4</sub>	11	0.954	8.35	1 798.4	0.87
<i>II</i> <sup>b</sup>	CHCl <sub>3</sub>	13	0.982	8.68	1 786.9	0.60
<i>III</i>	CCl <sub>4</sub>	9	0.979	6.13	1 799.3	0.49
<i>III</i> <sup>b</sup>	CHCl <sub>3</sub>	10	0.979	7.45	1 787.0	0.70

<sup>a</sup> Data taken from ref. <sup>1</sup> <sup>b</sup> Data taken from ref. <sup>2</sup>

$\nu(\text{C}=\text{O})$  vs  $\sigma$  type correlations for a series of compounds containing a 3- or 4-substituted phenyl group are practically identical with those of the corresponding series of compounds containing a 4-substituted naphthyl group. Consequently, the  $\sigma_{Ar}$  constants for the 4-substituted 1-naphthyl groups may be calculated from equation (1)



$$\sigma_{Ar}(4\text{-X-1-Naph}) = \sigma_p - 0.09, \quad (1)$$

where  $\sigma_p$  are the Hammett constants<sup>14</sup> for 4-substituted phenyl groups and 0.09 is the  $\sigma_{Ar}$  constant for 1-naphthyl group. As it may be seen from Fig. 1, these newly calculated  $\sigma_{Ar}(4\text{-X-1-Naph})$  constants for the 4-substituted 1-naphthyl groups are well in accord with the linear  $\nu(\text{C}=\text{O})$  vs  $\sigma$  correlations in the case of compounds I.

The slopes of the linear  $\nu(\text{C}=\text{O})$  vs  $\sigma$  correlations from Table III were used in calculations of transmissive factors of substituent effects for the —O— and —S— bridges in tetrachloromethane on the basis of equations  $\pi'(\text{O}) = \varrho_{II}/\varrho_{III}$  and  $\pi'(\text{S}) = \varrho_{III}/\varrho_I$  where  $\varrho_I$ ,  $\varrho_{II}$ , and  $\varrho_{III}$  are slopes of the linear  $\nu(\text{C}=\text{O})$  vs  $\sigma$  correlations for the series of compounds I, II, and III, resp. Table IV shows the transmissive factors  $\pi'(\text{O})$  and  $\pi'(\text{S})$  in tetrachloromethane along with the transmissive factors determined<sup>2</sup> in chloroform. For the sake of comparison, Table IV also contains the  $\pi'(\text{Fu})$  and  $\pi'(\text{Thi})$  transmissive factors for the 2,5-furylene and 2,5-thienylene bridge as determined<sup>8</sup> in chloroform and tetrachloromethane. It may be seen from Table IV that the transmission of substituent effects by the oxygen bridge is more efficient in tetrachloromethane than in chloroform. On the other hand, the solvent does not affect

TABLE IV

Effect of Solvents on Transmissive Factors of the Oxygen Atom and Sulfur Atom-Containing Bridges

Bridge	Solvent	$\pi'$	$\pi'_{\text{calc.}}^a$	$\Delta\pi'/\pi'^b$
—O—	$\text{CHCl}_3$	0.72 <sup>c</sup>	—	0.163
	$\text{CCl}_4$	0.86	—	
—S—	$\text{CHCl}_3$	0.62 <sup>c</sup>	—	0.016
	$\text{CCl}_4$	0.63	—	
	$\text{CHCl}_3$	0.47 <sup>d</sup>	0.52	0.266
	$\text{CCl}_4$	0.64 <sup>d</sup>	0.59	
	$\text{CHCl}_3$	0.42 <sup>d</sup>	0.48	0.045
	$\text{CCl}_4$	0.44 <sup>d</sup>	0.48	

<sup>a</sup> Calculated from equation (3) and (4), resp. <sup>b</sup> Calculated from equation (2). <sup>c</sup> Data taken from ref.<sup>2</sup> <sup>d</sup> Data taken from ref.<sup>8</sup>.

the transmission of substituent effects by the sulfur bridge. A similar result has been obtained<sup>4-8</sup> in investigations on the influence of solvents on the transmission of substituent effects by the 2,5-furylene and 2,5-thienylene bridge (Table IV). The influence of the solvent on the transmission of substituent effects by the oxygen bridge might be explained analogously to the 2,5-furylene bridge, *i.e.*, by the formation of a hydrogen bonding between the transmission center (the oxygen atom) and the hydrogen atom of the solvent (chloroform). On the other hand, in the case of the sulfur bridge the molecules of chloroform do not affect the transmission of substituent effects because of the decreased ability of the sulfur atom to form hydrogen bondings; consequently, the  $\pi'(S)$  transmission factor is in chloroform practically identical with that in tetrachloromethane, *i.e.*, an aprotic solvent which does not form hydrogen bondings. The influence of the solvent on the  $\pi'(O)$ ,  $\pi'(S)$ ,  $\pi'(Fu)$ , and  $\pi'(Thi)$  transmissive factors is expressed in Table IV by the  $\Delta\pi'/\pi'$  values defined in equation (2)

$$\Delta\pi'/\pi' = (\pi'_{CCl_4} - \pi'_{CHCl_3})/\pi'_{CCl_4}, \quad (2)$$

where  $\pi'_{CCl_4}$  and  $\pi'_{CHCl_3}$  are transmissive factors for the particular bridge in tetrachloromethane and chloroform, resp.

The transmissive factors for the —O— and —S— bridges may be envisaged as  $\varepsilon(O)$  and  $\varepsilon(S)$  partial transmissive factors for the corresponding —O— and —S— bond centers and may be used in calculations of transmissive factors for more complex systems. Table IV contains the  $\pi'_{calc.}$  transmissive factors calculated for the 2,5-furylene and 2,5-thienylene bridge with the use of equations (3) and (4)

$$\pi'(Fu)_{calc.} = \varepsilon^4(C_{sp^2}) + \varepsilon^2(C_{sp^2}) \varepsilon(O), \quad (3)$$

$$\pi'(Thi)_{calc.} = \varepsilon^4(C_{sp^2}) + \varepsilon^2(C_{sp^2}) \varepsilon(S), \quad (4)$$

where  $\varepsilon(C_{sp^2}) = 0.67$  is transmissive factor for a  $sp^2$  hybridized carbon atom as determined by Bowden<sup>17</sup> and  $\varepsilon(O)$  and  $\varepsilon(S)$  are the corresponding  $\pi'(O)$  and  $\pi'(S)$  transmissive factors from Table IV. As it may be seen from comparison of data in Table IV, the  $\pi'_{calc.}$  transmissive factors obtained from equations (3) and (4) are in good accord with the  $\pi'(Fu)$  and  $\pi'(Thi)$  transmissive factors determined by the earlier experiments<sup>4-8</sup>.

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