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INFRARED SPECTRA OF SUBSTITUTED 5-PHENYL-2-THIOPHENECARBOXALDEHYDES AND 2-(5-PHENYL-2-THENYLIDENE)-1,3-INDANDIONES

TRANSMISSION OF POLAR EFFECTS BY THE THIOPHENE RING

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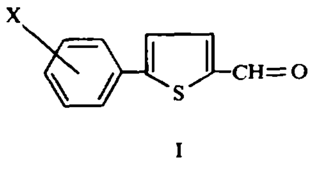
Abstract—Hammett correlations between the C═O stretching frequencies and substituent constants were studied for a series of 5-phenyl-2-thiophenecarboxaldehydes and 2-(5-phenyl-2-thenylidene)-1,3-indandiones and compared with those for a series of benzaldehydes and 2-benzylidene-1,3-indandiones. From the slopes of the statistically most significant relationships the transmissive factors for the thiophene ring in carbon tetrachloride and chloroform were calculated. Transmission by the thiophene ring is practically independent of solvent contrary to transmission by the furan ring, where the transmissive center interacts with solvent molecules. From a comparison of transmissive factors it was found that the efficiency of transmission by the bridging groups decreases in the order furan > thiophene > benzene *i.e.* in the order in which the delocalization energies of these systems increase. The preparation of nine new 2-(5-phenyl-2-thenylidene)-1,3-indandiones is also described.

IN PRECEDING WORK[1,2] we have quantitativly investigated transmission of polar effects by the furan ring using Hammett correlations between the C═O stretching frequencies and substituent constants in series of substituted 2-(5-phenyl-2-furfurylidene)-1,3-indandiones and 5-phenyl-2-furaldehydes.

This paper deals with transmission of polar effects by the thiophene ring in comparison with the furan and benzene rings. For this purpose we compare linear correlations between the carbonyl stretching frequencies and substituent constants for a series of substituted 5-phenyl-2-thiophenecarboxaldehydes (I) and 2-(5-phenyl-2-thenylidene)-1,3-indandiones (II) with those for a series of substituted benzaldehydes (III)[2] and 2-benzylidene-1,3-indandiones (IV).[1]



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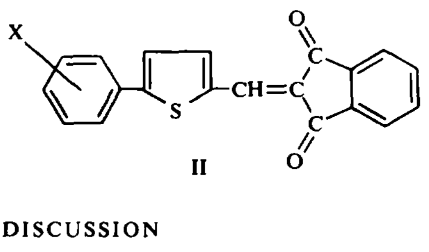

II

RESULTS AND DISCUSSION

The C═O stretching frequencies measured in CCl_4 and $CHCl_3$ for a series of 5-phenyl-2-thiophenecarboxaldehydes (I) are listed in Table 1. Comparison with the

TABLE 1. THE C=O STRETCHING FREQUENCIES AND CORRESPONDING σ SUBSTITUENT CONSTANTS FOR SUBSTITUTED 5-PHENYL-2-THIOPHENECARBOXALDEHYDES (I)

Compound	X	ν (cm^{-1})		σ
		CCl_4	$CHCl_3$	
1	4-OMe	1676	1664	−0·27
2	4-Me	1678	1666	−0·17
3	3-Me	1678	1667	−0·07
4	H	1679	1668	0·00
5	4-Br	1681	1671	0·23
6	4-Cl	1681	1671	0·23
7	3-Br	1681	1671	0·39
8	3-NO_2	—	1674	0·71
9	4-NO_2	1682	1675	0·78

spectral data for 5-phenyl-2-furaldehydes[2] shows that exchange of the furan ring for the thiophene ring causes a decrease of 7–13 cm^{-1} in the C=O stretching frequency. This fact draws attention to the increased conjugation of the C=O bond in system I in comparison with the 5-phenyl-2-furaldehydes. Passing from CCl_4 to $CHCl_3$ we observe a decrease of 10–12 cm^{-1} in the C=O stretching frequencies of compounds I.

2-(5-Phenyl-2-thenylidene)-1,3-indandiones (II), in similar manner to other 1,3-indandione derivatives[3] display doubled carbonyl bands corresponding to the symmetrical (ν_s) and asymmetrical (ν_{as}) stretching mode of the 1,3-dicarbonyl system. Frequencies of these vibrational modes as well as their arithmetic means ($\bar{\nu}$) are given in Table 2. The differences between the symmetrical and asymmetrical frequencies

TABLE 2. THE C=O STRETCHING FREQUENCIES AND CORRESPONDING σ AND σ^+ SUBSTITUENT CONSTANTS FOR SUBSTITUTED 2-(5-PHENYL-2-THENYLIDENE)-1,3-INDANDIONES (II)

Compound	X	CCl_4 (cm^{-1})			$CHCl_3$ (cm^{-1})			σ	σ^+
		ν_s	ν_{as}	$\bar{\nu}$	ν_s	ν_{as}	$\bar{\nu}$		
10	4-NH_2	1725	1686	1705·5	1721	1679	1700·0	−0·66	−1·30
11	4-OH	1726	1687	1706·5	1721	1681	1701·0	−0·37	−0·92
12	4-OMe	1728	1687	1707·5	1723	1680	1701·5	−0·27	−0·78
13	4-Me	1729	1688	1708·5	1724	1682	1703·0	−0·17	−0·31
14	3-Me	1729	1688	1708·5	1725	1682	1703·5	−0·07	−0·07
15	H	1730	1689	1709·5	1725	1683	1704·0	0·00	0·00
16	4-Cl	1731	1689	1710·0	1726	1683	1704·5	0·23	0·11
17	4-Br	1731	1689	1710·0	1727	1683	1705·0	0·23	0·15
18	4-NO_2	1732	1691	1711·5	1729	1686	1707·5	0·78	0·79

($\Delta\nu = \nu_s - \nu_{as}$) are in the range 39–45 cm^{-1} and are similar to those of other 1,3-indandione derivatives[1,3] having a sp^2—hybridized C_2 atom. Passing from CCl_4 to $CHCl_3$ we observed a decrease of 3–7 cm^{-1} in the symmetrical as well as in the asymmetrical C=O frequencies. When comparing the spectral data of compounds

II (Table 2) with those of the corresponding 2-(5-phenyl-2-furfurylidene)-1,3-indandiones,[1] we found that exchange of the furan ring for thiophene ring causes in all cases a decrease in both the symmetrical and asymmetrical C=O frequencies. This observation indicates again the increase in conjugation of C=O bonds in system II compared with the 2-(5-phenyl-2-furfurylidene)-1,3-indandiones.

As with the other series of compounds,[1,2,4] so in the 5-phenyl-2-thiophenecarboxaldehydes (I) and 2-(5-phenyl-2-thenylidene)-1,3-indandiones (II) studied here, linear correlations exist between the carbonyl stretching frequencies and substituent constants. The statistical parameters of correlations of type ν *vs.* σ for compounds I are given in Table 3 and those of types $\bar{\nu}$ *vs.* σ, $\bar{\nu}$ *vs.* σ^+, ν_{as} *vs.* σ, ν_s *vs.* σ, ν_{as} *vs.* σ^+ and and ν_s *vs.* σ^+ for compounds II are presented in Table 4. It can be seen from Table 4 that the statistically most significant correlations are of type $\bar{\nu}$ *vs.* σ^+. This observation is in a good agreement with the results of our preceding work.[1]

TABLE 3. STATISTICAL PARAMETERS OF HAMMETT CORRELATIONS OF TYPE ν *vs.* σ FOR SUBSTITUTED 5-PHENYL-2-THIOPHENECARBOXALDEHYDES (I)

Solvent	n^a	r^b	ρ^c	s_ρ^d	q^e	s_q^f	s^g
$CHCl_3$	9	0·980	9·69	0·74	1667·7	0·5	0·77
CCl_4	8	0·915	5·55	1·00	1678·7	0·4	0·90

[a] Number of compounds used in the correlation.
[b] Correlation coefficient.
[c] Slope.
[d] Error of the slope.
[e] Intercept (calculated value for the unsubstituted compound).
[f] Error of the intercept.
[g] Standard deviation.

TABLE 4. STATISTICAL PARAMETERS OF HAMMETT CORRELATIONS FOR SUBSTITUTED 2-(5-PHENYL-2-THENYLIDENE)-1.3-INDANDIONES (II)

Solvent	Correlation	n	r	ρ	s_ρ	q	s_q	s	$\bar{r}^a$
$CHCl_3$	$\bar{\nu}$ *vs.* σ.	9	0·985	5·43	0·36	1703·5	0·0	0·43	0·973
	$\bar{\nu}$ *vs.* σ^+	9	0·991	3·54	0·18	1704·2	0·1	0·32	0·990
	ν_{as} *vs.* σ	9	0·964	4·70	0·49	1682·3	0·0	0·57	0·956
	ν_s *vs.* σ	9	0·903	4·97	0·90	1724·5	0·1	1·01	0·935
	ν_{as} *vs.* σ^+	9	0·965	3·05	0·31	1682·9	0·2	0·57	0·977
	ν_s *vs.* σ^+	9	0·950	3·39	0·42	1725·2	0·3	0·77	0·968
CCl_4	$\bar{\nu}$ *vs* σ	9	0·966	4·38	0·44	1708·8	0·0	0·52	0·960
	$\bar{\nu}$ *vs.* σ^+	9	0·985	2·89	0·19	1709·4	0·1	0·34	0·976
	ν_{as} *vs.* σ	9	0·979	3·49	0·27	1688·3	0·0	0·32	0·950
	ν_s *vs.* σ	9	0·933	5·26	0·77	1729·2	0·1	0·90	0·951
	ν_{as} *vs.* σ^+	9	0·978	2·26	0·18	1688·8	0·1	0·33	0·964
	ν_s *vs.* σ^+	9	0·965	3·52	0·36	1729·9	0·3	0·66	0·969

[a] Arithmetic mean of correlation coefficients for the corresponding correlations in series of substituted 2-(5-phenyl-2-thenylidene)-1,3-indandiones (II) and 2-benzylidene-1,3-indandiones (IV).[1]

For other symbols see Table 3.

Using data in Table 3 and 4 we calculated the transmissive factors of the polar effects for the thiophene ring (more exactly the 2,5-thienylene bridge) π' (Thi) from equations:

$$\pi' \text{(Thi)} = \rho_I/\rho_{III} \qquad (1)$$

$$\pi' \text{(Thi)} = \rho_{II}/\rho_{IV} \qquad (2)$$

where ρ_I and ρ_{III} are the slopes of the ν *vs.* σ correlations for the series of substituted 5-phenyl-2-thiophenecarboxaldehydes (I) and benzaldehydes (III)[2] respectively and ρ_{II} and ρ_{IV} are the slopes of the $\bar{\nu}$ *vs.* σ^+ correlations for the series of substituted 2-(5-phenyl-2-thenylidene)-1,3-indandiones (II) and 2-benzylidene-1,3-indandiones (IV)[1] respectively. For calculation of the π' (Thi) values from eq. 2, the slopes of the $\bar{\nu}$ *vs.* σ^+ correlations were chosen. This choice, as in preceding works,[1,4] was carried out using the highest value of the arithmetic means of the correlation coefficients $\bar{r} = (r_{II} + r_{IV})/2$ for the corresponding correlations in a series of compounds of types II and IV (Table 4). The Hammett correlations, the slopes of which were used in eqs. 1 and 2 are in Figs 1 and 2 respectively.

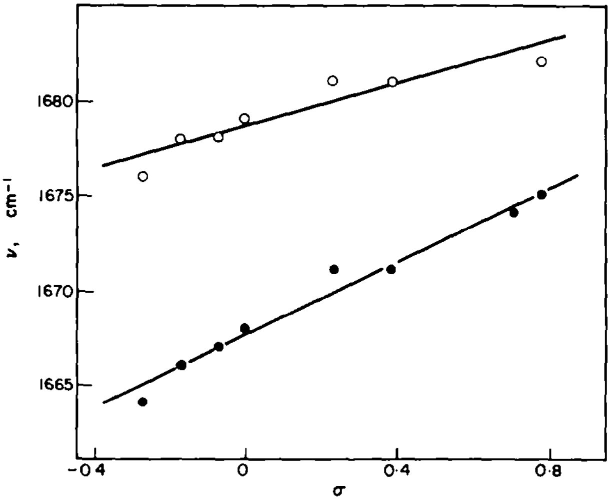

FIG 1. Plot of the C=O stretching frequencies *vs.* σ substituent constants for 5-phenyl-2-thiophenecarboxaldehydes (I): ○ –CCl_4, ● –$CHCl_3$

The transmissive factors π' (Thi) in both CCl_4 and $CHCl_3$ calculated from eqs. 1 and 2 are listed in Table 5. For comparison we have also included in this Table the transmissive factors for the thiophene and furan rings (2,5-furylene bridge) π' (Fu) presented in our preceding papers.[1,2,4] As the transmissive factors determined from the correlations for the three various systems are in a good agreement, we can express them by the mean values: $\bar{\pi}'$ (Thi and $\bar{\pi}'$ (Fu) (Table 5). From a comparison of the $\bar{\pi}'$ (Thi) and $\bar{\pi}'$ (Fu) values in CCl_4 with those in $CHCl_3$ it follows that the transmission of polar effects by the thiophene ring is practically independent of solvent. However, transmission by the furan ring is more efficient in CCl_4 than in $CHCl_3$. The cause of

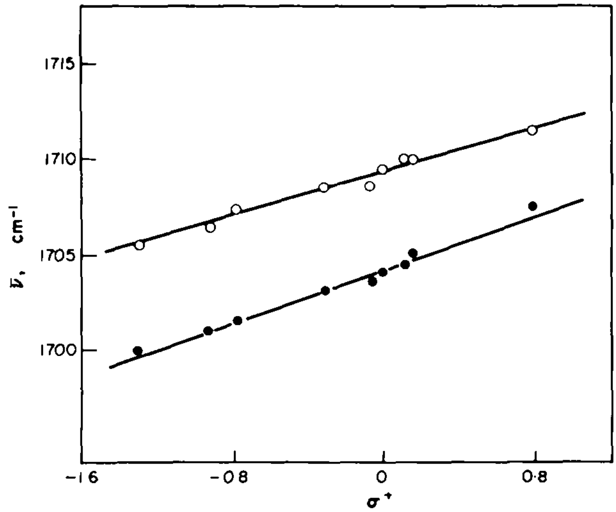

FIG 2. Plot of the arithmetic means of the symmetrical and asymmetrical C=O stretching frequencies *vs.* σ^+ substituent constants for 2-(5-phenyl-2-thenylidene)-1,3-indandiones (II): ○—CCl_4, ●—$CHCl_3$.

this was explained earlier[1] as hydrogen bonding between the oxygen atom of the furan ring and the chloroform molecules. In the case of the thiophene ring the small influence of solvent on transmission may be attributed to a lower hydrogen bonding ability of the thiophene ring sulphur atom in comparison with that of the furan ring oxygen atom.

TABLE 5. TRANSMISSIVE FACTORS OF THE POLAR EFFECTS FOR THIOPHENE AND FURAN RINGS

Solvent	π' (Thi)	$\bar{\pi}$ (Thi)	π' (Fu)	$\bar{\pi}'$ (Fu)
$CHCl_3$	0·40 ± 0·07[a] 0·40 ± 0·04[b] 0·37 ± 0·06[c]	0·39 ± 0·06	0·48 ± 0·06[d] 0·46 ± 0·05[e] 0·43 ± 0·09[f]	0·46 ± 0·07
CCl_4	0·40 ± 0·12[a] 0·47 ± 0·07[b] 0·45 ± 0·07[c]	0·44 ± 0·09	0·65 ± 0·12[d] 0·68 ± 0·12[e] 0·60 ± 0·12[f]	0·64 ± 0·12

Calculated from the slopes of the Hammett correlations:

[a] For 5-phenyl-2-thiophenecarboxaldehydes (I).

[b] For 2-(5-phenyl-2-thenylidene)-1,3-indandiones (II).

[c] For 2-(5-phenyl-2-thenylidene)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones.[4]

[d] For 5-phenyl-2-furaldehydes[2].

[e] For 2-(5-phenyl-2-furfurylidene)-1,3-indandiones.[1]

[f] For 2-(5-phenyl-2-furfurylidene)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones.[4]

As for the furan ring,[1] so for the thiophene ring it is possible to express the transmissive factor as an exponential function of transmissive factors for individual link centers:

$$\pi' (\text{Thi}) = \varepsilon^4 (C_{sp^2}) + \varepsilon^2 (C_{sp^2})\, \varepsilon (S) \qquad (3)$$

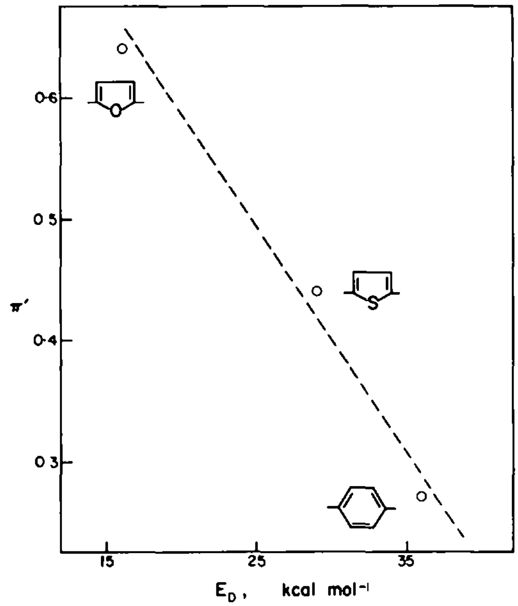

Fig 3. Plot of the transmissive factors of polar effects *vs.* delocalization energies for the furan, thiophene and benzene rings.

where $\varepsilon(C_{sp^2})$ and $\varepsilon(S)$ are apparent transmissive factors for the sp^2-hydridized carbon atom and for the sulphur atom respectively. If we use in eq. 3 the value of $\varepsilon(C_{sp^2})$ determined by Bowden[5] and the value of $\varepsilon(S)$ obtained earlier,[6] we obtain the value π' (Thi) = 0·48. It is evident that this calculated value is in a good agreement with the values π' (Thi) = 0·44 and π' (Thi) = 0·39 determined from the experimental measurements in CCl_4 and $CHCl_3$ respectively.

Comparing the values of the transmissive factors for the thiophene and the furan ring (determined in CCl_4 *i.e.* in the solvent which practically does not interact with the transmissive center) with that for the benzene ring[7] (*i.e.* for 1,4-phenylene bridge)

Table 6. Substituted 2-(5-phenyl-2-thenylidene)-1,3-indandiones (II)

X	Analysis % Calc			Analysis % Found			Formula	m.p.	Yield %
	C	H	S	C	H	S			
4-NH_2	72·49	3·95	9·67	72·56	4·12	9·83	$C_{20}H_{13}O_2S$	247–249	75
4-OH	72·27	3·64	9·64	72·13	3·51	9·43	$C_{20}H_{12}O_3S$	308–310	80
4-OMe	72·81	4·07	9·25	72·64	4·31	9·36	$C_{21}H_{14}O_3S$	198–200	91
4-Me	76·34	4·27	9·70	76·21	4·35	9·61	$C_{21}H_{14}O_2S$	191–192	89
3-Me	76·34	4·27	9·70	76·36	4·38	9·53	$C_{21}H_{14}O_2S$	149–151	89
H	75·93	3·82	10·13	75·87	3·96	10·23	$C_{20}H_{12}O_2S$	188–190	92
4-Cl	68·47	3·16	9·14	68·58	3·36	9·34	$C_{20}H_{11}ClO_2S$	241–243	93
4-Br	60·77	2·80	8·12	60·53	2·96	8·32	$C_{20}H_{11}BrO_2S$	263–266	89
4-NO_2	66·47	3·07	8·87	66·34	2·92	8·97	$C_{20}H_{11}NO_4S$	278–280	87

$\bar{\pi}'(\mathrm{Ph}) = 0{\cdot}27 \pm 0{\cdot}03$, we observe that the efficiency of transmission by the bridging groups decreases in the order furan > thiophene > benzene *i.e.* the order in which the delocalization energies of these systems increase. The same order of sensitivity to substituent effects was found by Marino *et al.*[8] for the furan, pyrrole, thiophene and benzene rings by determination of the molecular ionization potentials. From Fig. 3 it is possible to see that there probably exists a nearly linear relation between the values of the transmissive factors for 1,4-benzene and 2,5-five-membered heteroaromatic bridges and the corresponding delocalization energies of these systems.

EXPERIMENTAL

The 5-phenyl-2-thiophenecarboxaldehydes (I) have been prepared by a modified Meerwein method[9] and purified by repeated crystallization from EtOH prior to application.

The 2-(5-phenyl-2-thenylidene)-1,3-indandiones (II) with the exception of the 4-amino and 4-hydroxy derivatives were prepared analogously to 2-benzylidene-1,3-indandiones[10] *i.e.* by condensation of 1,3-indandione with the corresponding 5-phenyl-2-thiophenecarboxaldehydes in 96% EtOH aq, piperidine as catalyst. The 2-[5-(4-aminophenyl)-2-thenylidene]-1,3-indandione was obtained from the corresponding 4-nitro derivative by reduction with $SnCl_2$ in AcOH.[11] 2-[5-(4-Hydroxyphenyl)-2-thenylidene]-1,3-indandione was prepared by the Zeisel reaction *i.e.* hydrolysis of the corresponding 4-methoxy derivative in 37% HBr aq. All compounds of type II except the 4-amino derivative were purified by repeated crystallization from AcOH, 2-[5-(4-aminophenyl)-2-thenylidene]-1,3-indandione was crystallized from acetone. As 2-(5-phenyl-2-thenylidene)-1,3-indandiones (II) studied have not been described previously, we give m.ps and analytical data in Table 6.

IR spectra were recorded on a Zeiss UR 20 spectrophotometer in the 1800–1600 cm^{-1} region; calibrated by a standard mixture of indene, camphor and cyclohexanone[12] (accuracy $\pm 0{\cdot}5\ cm^{-1}$). The solvents, CCl_4 and $CHCl_3$, both of analytical purity were purified and dried in the usual manner. NaCl cells with path lengths 0·1 cm, 0·5 cm and 1 cm were used. Solution concentrations were chosen to give absorption between 70–75%.

In Hammett correlations σ substituent constants reported by McDaniel and Brown[13] and σ^+ constants published by Brown and Okamoto[14] were used. The parameters of linear correlations were computed on a Regnezentralen Gier computer using non-approximated statistical relations.[15]

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