Tetrahedron Vol. 28, pp. 1025 to 1032. Pergamon Press 1972. Printed in Great Britain

INFRARED SPECTRA OF SUBSTITUTED 2-(5-PHENYL-2-FURFURYLIDENE)-1,3-INDANDIONES AND TRANSMISSION OF POLAR EFFECTS BY THE FURAN RING

A. PERJÉSSY, P. HRNČIAR

Department of Organic Chemistry, Komensky University, Bratislava, Czechoslovakia

and

A. KRUTOŠÍKOVÁ

Department of Organic Chemistry, Slovak Technical University, Bratislava, Czechoslovakia

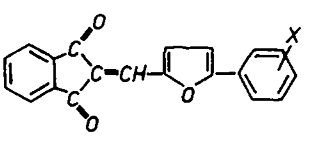
(*Received in the UK* 2 *September* 1971; *Accepted for publication* 28 *October* 1971)

Abstract—The C=O stretching frequencies of substituted 2-(5-phenyl-2-furfurylidene)-1,3-indandiones in carbon tetrachloride and chloroform were compared with those of substituted 2-benzylidene-1,3-indandiones. The Hammett correlations between the symmetrical, asymmetrical, arithmetic means of symmetrical and asymmetrical C=O stretching frequencies and σ as well as σ^+ substituent constants were statistically evaluated in both series. From the statistically most significant correlations, *i.e.* from the correlations between the arithmetic means of the symmetrical and asymmetrical C=O stretching frequencies and σ^+ constants, the transmissive factors for furan ring in carbon tetrachloride and in chloroform were calculated. A decrease in the value of the transmissive factor in chloroform is probably caused by hydrogen bonding between oxygen atom of the furan ring and chloroform molecules. The value of the transmissive factor for furan ring determinated in chloroform is in very good agreement with that calculated from the values of apparent transmissive factors for individual link centers. The preparation of eleven new 2-(5-phenyl-2-furfurylidene)-1,3-indandiones is also described.

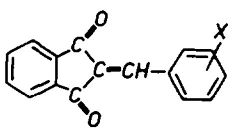
LINEAR CORRELATIONS between the C=O stretching frequencies and substituent constants with compounds containing a bridge atom or group between a substituted benzene ring and carbonyl group can be used in quantitative study of the transmission of polar effects by the given bridge atom or group.

In preceding work[1-5] using this method we investigated the transmission of polar effects by simple groups and atoms. We have studied[6] the IR spectra of substituted 2-benzylidene-1,3-indandiones and found a linear correlation between the arithmetic means of symmetrical and asymmetrical C=O stretching frequencies and σ^+ substituent constants. Kaneti and Yuchnovski,[7] have investigated for 2-benzylidene-1,3-indandiones Hammett correlations of the types ν_s(C=O) *vs.* σ^+ and ν_{as}(C=O) *vs.* σ^+ as well as the transmission of polar effects by the —CH=CH— grouping in a series of 2-cinnamylidene-1,3-indandiones. Although a number of papers have been published on transmission of polar effects, however, transmission by the furan ring has not yet been studied.

Here we use Hammett correlations between the arithmetic means of symmetrical and asymmetrical C=O stretching frequencies and σ^+ constants in series of substituted 2-(5-phenyl-2-furfurylidene)-1,3-indandiones (I) and 2-benzylidene-1,3-indandiones (II) for a quantitative study of the transmission of polar effects by the furan ring.



I



II

RESULTS AND DISCUSSION

It is known that 1,3-indandione derivatives[8] display doubled C=O stretching bands. The more intense lower frequency band was assigned to the asymmetrical and the less intense higher frequency band to the symmetrical stretching mode of the 1,3-dicarbonyl grouping.[7, 8]

The symmetrical (ν_s), and asymmetrical (ν_{as}) C=O stretching frequencies measured in CCl_4 and $CHCl_3$, as well as the arithmetic means of both frequencies ($\bar{\nu}$) for substituted 2-(5-phenyl-2-furfurylidene)-1,3-indandiones (I) are given in Table 1. The differences between the symmetrical and asymmetrical frequencies ($\Delta\nu = \nu_s - \nu_{as}$) are in the range of 39 – 40 cm^{-1}, and are similar to those of other 1,3-indandione derivatives[8] having a sp^2-hybridized C_2 atom. Passing from CCl_4 to $CHCl_3$ we observe the increase of 3 – 5 cm^{-1} in the symmetrical frequency and of 6 – 8 cm^{-1} in the asymmetrical frequency, thereby showing a higher sensitivity of the latter to solvent effects. A similar observation was made with substituted 2-benzylidene-1,3-indandiones (II).[6] When comparing the frequencies of substituted 2-(5-phenyl-2-furfurylidene)-1,3-indandiones (I) with those of the corresponding 2-benzylidene-1,3-indandiones (II),[6] we found that the furan ring in all cases causes a decrease in the

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

Compound No.	X	CCl_4			$CHCl_3$				
		ν_s	ν_{as}	$\bar{\nu}$	ν_s	ν_{as}	$\bar{\nu}$	σ	σ^+
1	4-NH_2	[a]	[a]	[a]	1722	1675	1698·5	−0·66	−1·30
2	4-OMe	1728	1686	1707·0	1724	1680	1702·0	−0·27	−0·78
3	4-Me	1729	1688	1708·5	1726	1681	1703·5	−0·17	−0·31
4	H	1729	1690	1709·5	1726	1682	1704·0	0·00	0·00
5	4-Br	1731	1690	1710·5	1727	1683	1705·0	0·23	0·15
6	4-Cl	1731	1690	1710·5	1726	1682	1704·0	0·23	0·11
7	3-F	1731	1690	1710·5	1728	1683	1705·5	0·34	0·35
8	3-Cl	1732	1691	1711·5	1728	1683	1705·5	0·37	0·40
9	3-Br	1731	1691	1711·0	1728	1684	1706·0	0·39	0·40
10	3-NO_2	1733	1693	1713·0	1729	1686	1707·5	0·71	0·67
11	4-NO_2	1734	1694	1714·0	1729	1687	1708·0	0·78	0·79

The frequencies are given in cm^{-1}.

[a] The values could not be measured owing to very low solubility of the compound in CCl_4.

TABLE 2. STATISTICAL PARAMETERS OF HAMMETT CORRELATIONS FOR SUBSTITUTED 2-(5-PHENYL-2-FURFFURYLIDENE)-1,3-INDANDIONES (I) AND TRANSMISSIVE FACTORS OF POLAR EFFECTS FOR THE FURAN RING

Solvent	Correlation	n^a	r^b	ρ^c	s_ρ^d	q^e	s_q^f	s^g	$\bar{r}^h$	$\pi'(Fu)^i$
CHCl$_3$	$\bar{\nu} - \sigma$	11	0·976	6·04	0·45	1703·4	0·3	0·61	0·969	0·46
	$\bar{\nu} - \sigma^+$	11	0·981	4·13	0·27	1704·3	0·0	0·53	0·985	0·46
	$\nu_{as} - \sigma$	11	0·968	7·21	0·62	1681·1	0·4	0·83	0·958	0·51
	$\nu_s - \sigma$	11	0·962	4·87	0·46	1725·8	0·3	0·62	0·965	0·38
	$\nu_{as} - \sigma^+$	11	0·963	4·87	0·46	1682·2	0·1	0·90	0·971	0·51
	$\nu_s - \sigma^+$	11	0·983	3·39	0·21	1726·5	0·0	0·42	0·984	0·40
CCl$_4$	$\bar{\nu} - \sigma$	10	0·982	5·84	0·40	1709·1	0·3	0·40	0·968	0·58
	$\bar{\nu} - \sigma^+$	10	0·971	4·24	0·37	1709·8	0·2	0·51	0·972	0·68
	$\nu_{as} - \sigma$	10	0·958	6·37	0·67	1688·6	0·6	0·69	0·939	0·67
	$\nu_s - \sigma$	10	0·976	5·31	0·42	1729·5	0·3	0·43	0·969	0·55
	$\nu_{as} - \sigma^+$	10	0·971	4·74	0·41	1689·5	0·2	0·58	0·966	0·77
	$\nu_s - \sigma^+$	10	0·937	3·74	0·49	1730·2	0·3	0·69	0·955	0·60

[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. [h] Arithmetic mean of the correlation coefficients for series of compound I and II. [i] Transmissive factor of polar effects for furan ring.

symmetrical as well as in the asymmetrical C=O frequency. This fact draws attention to prolongation of conjugation of C=O bonds in the system of 2-(5-phenyl-2-furfurylidene)-1,3-indandiones (I).

As in the case of substituted 2-benzylidene-1,3-indandiones,[6, 7] so also in the series of 2-(5-phenyl-2-furfurylidene)-1,3-indandiones (I) we expect the validity of linear correlations between the carbonyl frequencies and substituent constants. In Table 2 the statistical parameters of Hammett correlations of types $\bar{\nu}$ *vs.* σ, $\bar{\nu}$ *vs.* σ^+, ν_{as} *vs.* σ, ν_s *vs.* σ, ν_{as} *vs.* σ^+ and ν_s *vs.* σ^+ calculated from data measured in CCl_4 and $CHCl_3$ are given for substituted 2-(5-phenyl-2-furfurylidene)-1,3-indandiones (I). In Table 3, for comparison, the statistical parameters of the same correlations for 2-benzylidene-1,3-indandiones (II) are listed, calculated from results published in a preceding paper.[6] Comparing the data given in Table 2 and Table 3 we found in most cases that the linear correlations are statistically more significant, when Brown and Okamoto's σ^+ constants[9] are used. This observation is also in agreement with results of preceding papers.[6, 7]

TABLE 3. STATISTICAL PARAMETERS OF HAMMETT CORRELATIONS FOR SUBSTITUTED 2-BENZYLIDENE-1,3-INDANDIONES (II)

Solvent	Correlation	n	r	ρ	s_ρ	q	s_q	s
$CHCl_3$	$\bar{\nu} - \sigma$	10	0·962	13·23	1·33	1708·4	0·3	2·27
	$\bar{\nu} - \sigma^+$	10	0·989	8·91	0·47	1710·8	0·2	1·23
	$\nu_{as} - \sigma$	10	0·948	14·16	1·69	1686·9	0·4	2·87
	$\nu_s - \sigma$	10	0·968	12·70	1·16	1730·0	0·3	1·97
	$\nu_{as} - \sigma^+$	10	0·980	9·59	0·69	1689·5	0·3	1·78
	$\nu_s - \sigma^+$	10	0·986	8·47	0·51	1732·2	0·2	1·33
CCl_4	$\bar{\nu} - \sigma$	9	0·955	9·51	1·12	1713·9	0·0	1·75
	$\bar{\nu} - \sigma^+$	9	0·973	6·20	0·55	1715·5	0·4	1·36
	$\nu_{as} - \sigma$	9	0·921	9·35	1·50	1693·1	0·1	2·35
	$\nu_s - \sigma$	9	0·969	9·67	0·94	1734·8	0·0	1·47
	$\nu_{as} - \sigma^+$	9	0·951	6·18	0·76	1694·7	0·5	1·86
	$\nu_s - \sigma^+$	9	0·974	6·21	0·55	1736·4	0·4	1·35

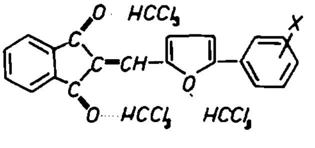
For denotation of symbols see Table 2.

In Table 2 there are also given the transmissive factors of polar effects for the furan ring $\pi'(Fu)$. calculated from equation:

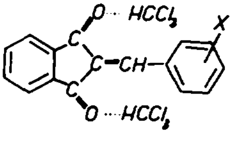
$$\pi'(Fu) = \sigma_I/\sigma_{II} \qquad (1)$$

where σ_I and σ_{II} are the slopes of the corresponding Hammett correlations for a series of compounds of type I and II respectively.

From the comparison of values $\pi'(Fu)$, determined from measurements in both solvents it can be concluded that polar effects are transmitted by furan rings in $CHCl_3$ solution less readily that in CCl_4. A probable explanation is that in $CHCl_3$ the molecules of compounds I and II are stabilized by hydrogen bonding between oxygen atoms and solvent molecules (III and IV). Whereas the transmission of polar effects in complexes III and IV is supported by polarization of the C=O bonds, participation of the p-electrons of the furan ring oxygen atom in further hydrogen bonding in complex III makes the transmission of polar effects by the furan ring more difficult. On the other hand, CCl_4 as an aprotic and non-polar solvent does not interact with the transmission center and therefore in this solvent the transmission may be considered, in first approximation to be uninfluenced by the medium.



III



IV

For the determination of statistically more significant values of transmissive factors $\pi'(Fu)$ in both solvents Hammett correlations of type $\bar{\nu}$ *vs.* σ^+ for a series of compounds of types I and II were chosen (Fig. 1). This selection was carried out on

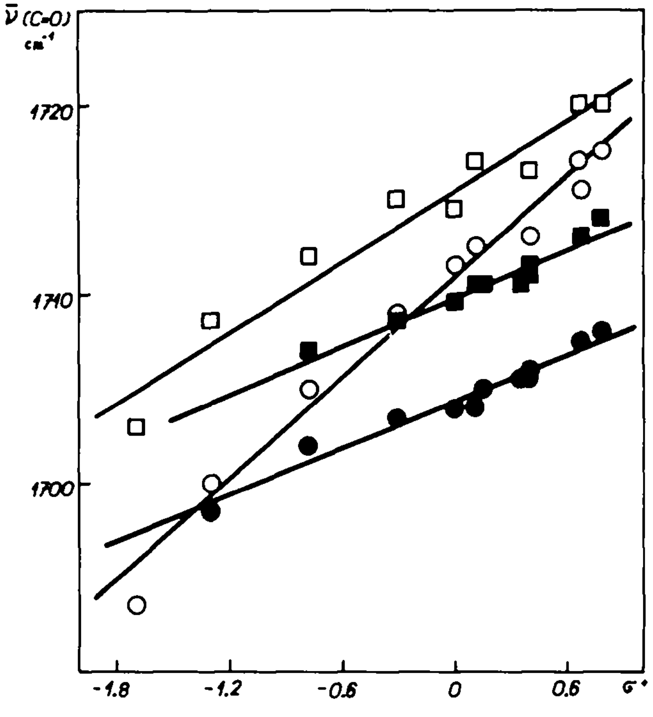


FIG 1. Plot of the arithmetic means of the symmetrical and asymmetrical C=O stretching frequencies vs. σ^+ substituent constants for 2-(5-phenyl-2-furfurylidene)-1,3-indandiones (I):

■—in carbon tetrachloride

●—in chloroform

for 2-benzylidene-1,3-indandiones (II):

□—in carbon tetrachloride

○—in chloroform

TABLE 4. SUBSTITUTED 2-(5-PHENYL-2-FURFURYLIDENE)-1,3-INDANDIONES (I)

X	Composition				Formula	m.p.	Yield	Crystallization
	Theory		Found					
	%C	%H	%C	%H			%	solvent
4-NH$_2$	76·18	4·16	76·31	3·96	$C_{20}H_{13}NO_3$	298–300	81	acetone
4-OMe	76·36	4·27	76·76	4·23	$C_{21}H_{14}O_4$	209–210	82	CHCl$_3$
4-Me	80·24	4·49	80·12	4·51	$C_{21}H_{14}O_3$	212 214	86	CHCl$_3$
H	79·99	4·03	79·73	3·78	$C_{20}H_{12}O_3$	226–228	91	EtOH
4-Br	63·35	2·92	63·94	2·73	$C_{20}H_{11}BrO_3$	239–241	87	acetone
4-Cl	71·76	3·31	71·64	3·38	$C_{20}H_{11}ClO_3$	290–291	93	CHCl$_3$
3-F	75·47	3·48	75·83	3·55	$C_{20}H_{11}FO_3$	268–269	92	CHCl$_3$
3-Cl	71·76	3·31	71·81	3·20	$C_{20}H_{11}ClO_3$	262–263	89	CHCl$_3$
3-Br	63·35	2·92	63·22	2·91	$C_{20}H_{11}BrO_3$	255–257	86	acetone
3-NO$_2$	69·57	3·21	69·31	3·23	$C_{20}H_{11}NO_5$	259–260	76	dioxan
4-NO$_2$	69·57	3·21	69·68	3·28	$C_{20}H_{11}NO_5$	290–291	78	dioxan

the basis of the highest value of arithmetic means of correlation coefficients $\bar{r} = (r_I + r_{II})/2$ for the corresponding correlation in a series of compounds of types I and II (Table 1). This approach leads to the value of the transmissive factor of polar effects for furan rings (more exactly for the 2,5-furylene bridge) $\pi'(Fu) = 0{\cdot}68 \pm 0{\cdot}12$ in CCl_4 and $\pi'(Fu) = 0{\cdot}46 \pm 0{\cdot}05$ in $CHCl_3$. When comparing the transmissive factor for the furan ring with that for the benzene ring[10–12] (1,4-phenylene bridge) we observe that the polar effects are transmitted by the furan ring approximately twice as readily as by the benzene ring.

It was shown[13–16] that it is possible to approximate the transmissive factor for some bridge group as an exponential function of the transmissive factors ε calculated for individual link centers of the given bridge group. Accordingly the transmissive factor for the furan ring can be expressed by:

$$\pi'(Fu) = \varepsilon^4(C_{sp^2}) + \varepsilon^2(C_{sp^2})\varepsilon(O) \qquad (2)$$

where $\varepsilon(C_{sp^2})$ and $\varepsilon(O)$ are apparent transmissive factors calculated for the sp^2-hybridized carbon atom and for the oxygen atom respectively.

If we use in Eq. 2 the values of ε determined by Bowden,[17] we obtain for the transmissive factors for the furan ring the value $\pi'(Fu) = 0{\cdot}47$. It is evident that this calculated value is in very good agreement with that $\pi'(Fu) = 0{\cdot}46 \pm 0{\cdot}05$ determined from the experimental measurements in $CHCl_3$ and that it is lower than the experimental value determined in CCl_4. The apparent transmissive factors ε for individual link centers have been calculated by Bowen[17] in most cases from measurements in media with hydrogen bonding ability. Comparing the experimental values of transmissive factors for groups containing an oxygen atom with those calculated from ε values, it was found that the experimental values were always higher than calculated, when they were determined in solvents without hydrogen bonding ability. For example, the transmissive factor for $—O—C_6H_4—$ group determined from the data measured in benzene[18] is approximately twice that calculated. On the other hand, the experimental value of the transmissive factor for the $—O—CH_2—$ group determined from measurements in aqueous or ethanolic media[17] is in very good agreement with the calculated value. Thus it can be concluded that the transmissive factors of groups containing atoms which are able to interact with solvents will be dependent on the nature of the solvent.

EXPERIMENTAL

The 2-(5-phenyl-2-furfurylidene)-1,3-indandiones (I) with the exception of 2-[5-(4-aminophenyl)-2-furfurylidene]-1,3-indandione were prepared analogously to 2-benzylidene-1,3-indandiones[19] *i.e.* by condensation of 1,3-indandione with the corresponding substituted 5-phenyl-2-furaldehydes in 90% ethanolic medium, piperidine as catalyst. 2-[5-(4-Aminophenyl)-2-furfurylidene]-1,3-indandione was obtained from 2-[5-(4-nitrophenyl)-2-furfurylidene]-1,3-indandione by reduction of the nitro group with $SnCl_2$ in AcOH according to the method described.[20] All compounds were purified by repeated crystallization from solvents listed in Table 4. As 2-(5-phenyl-2-furfurylidene)-1,3-indandiones (I) studied have not been described previously, we give m.ps and analytical data in Table 4.

The IR spectra were recorded on Zeiss UR20 spectrophotometer in the 1800 – 1600 cm^{-1} region. The instrument was calibrated by the standard spectrum of the mixture of indene, camphor and cyclohexanone.[21] The accuracy of the frequencies registered was ± 1 cm^{-1}. CCl_4 and $CHCl_3$, both of analytical purity were purified and dried in the usual manner. NaCl cells with path lengths 0·5 cm and 0·1 cm were used. Concentrations of solutions were chosen to give absorption between 70–75%.

In spectral data correlations σ substituent constants reported by McDaniel and Brown[22] and σ^+ constants published by Brown and Okamoto[9] were used. The parameters of linear correlations were computed on a Regnezentralen Gier digital computer using non-approximated statistical relations.[23]

REFERENCES

[1] A. Perjéssy and P. Hrnčiar, *Collect. Czechoslov. Chem. Comm.* **35**, 1120 (1970)
[2] A. Perjéssy and M. Lácová, *Ibid.* **36**, 2956 (1971)
[3] A. Perjéssy, M. Lácová and P. Hrnčiar, *Ibid.* **36**, 2775 (1971)
[4] A. Perjéssy, M. Vida, P. Hrnčiar and M. Lácová, *Ibid.* (in press)
[5] A. Perjéssy and P. Hrnčiar, *Ibid.* (in press)
[6] A. Perjéssy and D. Zacharová-Kalavská, *Ibid.* **35**, 3802 (1970)
[7] J. Kaneti and I. Juchnovski, *Tetrahedron* **26**, 4397 (1970)
[8] A. Perjéssy and P. Hrnčiar, *Ibid.* (in press)
[9] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.* **80**, 4979 (1958)
[10] Z. N. Parnes, V. I. Zhdanovitch and D. N. Kursanov, *Dokl. Akad. Nauk SSSR* **132**, 1322 (1960)
[11] V. D. Bezuglij, V. N. Dmitrijeva, I. A. Shkodina and L. A. Melnik, *Zhur. Obschei Khim.* **34**, 376 (1964)
[12] P. Zuman, *Chem. Listy* **48**, 94 (1954)
[13] J. G. McGowan, *J. Soc. Chem. Ind.* **68**, 253 (1949)
[14] J. McGowan, *J. Appl. Chem.* **10**, 312 (1960)
[15] O. Exner and J. Jonáš *Collect. Czechoslov. Chem. Comm.* **27**, 2296 (1960)
[16] R. W. Taft, *J. Phys. Chem.* **64**, 1805 (1960)
[17] K. Bowden, *Can. J. Chem.* **41**, 2781 (1963)
[18] L. M. Litvinenko, *Izvest. Akad. Nauk SSSR, Otd. Khim. Nauk* 1737 (1962)
[19] T. T. Dumpis and G. J. Vanag, *Izvest. Akad. Nauk Latv. SSR, Ser. Khim.* 241 (1961)
[20] P. Hrnčiar and J. Ulehla, *Chem. Zvesti* **23**, 59 (1969)
[21] R. N. Jones, P. K. Fauer and W. Zacharias, *Rev. Univers. Mines* **15**, 417 (1959)
[22] D. M. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958)
[23] J. Eichler, *Chem. Listy* **60**, 1203 (1966)