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APPLICATION OF THE SETH-PAUL-VAN DUYSE EQUATION—III[1]

TRANSMISSION OF POLAR EFFECTS BY THE FURAN RING

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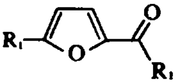
Abstract—The improved Seth-Paul-Van Duyse equation (SPVDE) has been used to determine transmissive factors of polar effects for the furan ring. The SPVDE was applied to the C=O stretching frequencies of O–O-*trans* and O–O-*cis* conformers of a series of substituted 5-phenyl-2-furancarbonyl compounds measured in carbon tetrachloride. The transmissive factors for furan ring in both conformation O–O-*trans* and O–O-*cis* have been calculated with a higher accuracy than found by using the methods described earlier. The applicability of the improved SPVDE to the 96 C=O stretching frequencies of various 5-phenyl-2-furancarbonyl compounds has been proved.

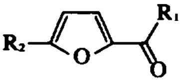
It has been shown[1] that the use of the improved SPVDE[2] provides a new statistically significant method for determination of transmissive factors of substituent effects for various bridge grous.

In the series of papers[3–7] the transmission of substituent effect by the furan and thiophene ring has been investigated on the basis of simple Hammett correlations. The number of compounds in the individual series used in these correlations varied from 8 to 12 and the transmissive factor for the furan ring (2,5-furylene bridge) of O–O-*trans* conformers of 5-phenyl-2-furancarbonyl compounds (in CCl_4) was found to be in the region of 0·59–0·68 and was determined with an accuracy from 11 to 20%.

The aim of this work was a further application of the improved SPVDE[2] in investigation of the transmission of substituent effects and the determination of a more accurate value of transmissive factor of polar effects for furan ring than found by methods described earlier.[3–8] For this purpose we measured as well as took from literature[5,7] the C=O stretching frequencies of a relatively large number of 5-phenyl-2-furancarbonyl compounds.



O-O-*trans*
I



O-O-*cis*
II

The CO stretching frequencies of O–O-*trans* (I) and O–O-*cis* (II) conformers of these compounds measured in CCl_4 together with corresponding $\Sigma X^+(R')$ values are listed in Table 1. The CO stretching frequencies were assigned to the O–O-*trans* and O–O-*cis* conformers according to the analogy from literature.[14–18] The $\Sigma X^+(R')$ values are defined in the scale of $X^+(R)$ constants[1,2,10] fitting the SPVDE, but neglecting the 2,5-furylene bridge group:

$$\sum X^+(R') = X^+(R_1) + X^+(R_2). \tag{1}$$

As the $X^+(R)$ constant of the CH=CHPh group in s-*cis* conformation with the respect of C=O group is lacking in the work,[1,2,10] we determined it using the C=O stretching frequencies of a series of 1-aryl-3-phenylpropenones[19] (i.e. substituted chalcones): $X^+(\text{s-}cis\text{-CH=CHPh}) = 1{\cdot}323$. When correlate the CO stretching frequencies of O–O-*trans* and O–O-*cis* conformers of 5-phenyl-2-furancarbonyl compounds (series I and II respectively) with corresponding $\Sigma X^+(R')$ constants (Table 1) we obtained the following empirical relationships:

$$\nu(CO)_{O\text{–}O\text{-}trans} = 30{\cdot}684 \sum X^+(R') + 1595{\cdot}433 \tag{2}$$

for 54 experimental points and

$$\nu(CO)_{O\text{–}O\text{-}cis} = 37{\cdot}421 \sum X^+(R') + 1591{\cdot}333 \tag{3}$$

for 42 experimental points.

The result is shown in Fig. 1 and the statistical treatment of correlations is listed in Table 2. It can be noted that C=O stretching frequencies of O–O-*trans* conformers of substituted 5-phenyl-2-furancarboxylic acids (compounds 9–22) do not obey the linear relationships $\nu(CO)_{O\text{–}O\text{-}trans}$ vs $\Sigma X^+(R')$ (eqn 2). The CO stretching

Table 1. Carbonyl stretching frequencies and $\Sigma X^+(R')$ and $\Sigma X^+(R)$ values for 5-phenyl-2-furancarbonyl compounds (I and II)

Compound	R_1^a	R_2^a	$\nu(CO)^b$		$\Sigma X^+(R')$	$\Sigma X^+(R)$	
			O–O–-trans	O–O–-cis		O–O–-trans	O–O–-cis
1	4-BrPh	Me	1683	1700	2.920	2.659	3.066
2	4-NO_2Ph	Me	1688	1703	3.072	2.781	3.214
3	4-NO_2Ph	Et	1687	1701	3.023	2.741	3.167
4	4-ClPh	Me	1683	1698	2.910	2.651	3.056
5	4-BrPh	Pr	1682	1698	2.864	2.614	3.011
6	4-ClPh	Et	1682	1699	2.861	2.611	3.008
7	4-ClPh	Pr	1682	1698	2.854	2.606	3.001
8	4-BrPh	Et	1683	1698	2.871	2.619	3.018
9	2-NO_2Ph	OH	1742^c	1757	4.570		4.681
10	2-BrPh	OH	1738^c	1751	4.420		4.534
11	2-ClPh	OH	1739^c	1751	4.335		4.451
12	2-OMePh	OH	1729^c	1741	3.980		4.103
13	3-NO_2, 4-ClPh	OH	1733^c	1748	4.369		4.484
14	3-CF_3, 4-ClPh	OH	1740^c	1756	4.334		4.450
15	3,4-Cl_2Ph	OH	1739^c	1755	4.305		4.422
16	3,5-Cl_2Ph	OH	1739^c	1755	4.374		4.489
17	3-CF_3Ph	OH	1738^c	1754	4.301		4.418
18	3-BrPh	OH	1738^c	1755	4.272		4.389
19	3-ClPh	OH	1738^c	1754	4.272		4.389
20	3-FPh	OH	1738^c	1753	4.260		4.378
21	Ph	OH	1736^c	1752	4.170		4.289
22	3-OMePh	OH	1736^c	1752	4.189		4.308
23	4-BrPh	OMe	1717	1739	3.883	3.432	4.008
24	4-ClPh	OMe	1718	1739	3.873	3.424	3.999
25	4-MePh	OMe	1712	1733	3.773	3.344	3.901
26	4-OMePh	OMe	1710	1732	3.661	3.254	3.791
27	2-NO_2Ph	OMe	1722	1741	4.240	3.719	4.358
28	2-BrPh	OMe	1719	1739	4.090	3.598	4.211
29	2-BrPh	OMe	1719	1739	4.005	3.530	4.128
30	3-BrPh	OMe	1718	1740	3.942	3.479	4.066
31	2-OMePh	OMe	1713	1732	3.650	3.245	3.780
32	2-NH_2Ph	OMe	1711	1730	3.660	3.253	3.790
33	3-NO_2, 4-ClPh	OMe	1721	1743	4.039	3.557	4.161
34	3,4-Cl_2Ph	OMe	1720	1740	3.975	3.506	4.099
35	3,5-Cl_2Ph	OMe	1721	1742	4.044	3.561	4.166
36	3-NO_2Ph	OMe	1721	1740	4.006	3.531	4.129
37	3-CF_3Ph	OMe	1720	1740	3.971	3.503	4.095
38	3-ClPh	OMe	1718	1738	3.942	3.479	4.066
39	3-FPh	OMe	1719	1741	3.930	3.470	4.054
40	Ph	OMe	1715	1736	3.840	3.398	3.966
41	3-NH_2Ph	OMe	1715	1737	3.809	3.373	3.936
42	3-CF_3, 4-Cl	OMe	1726^c	1743	4.004		4.127
43	4-OMePh	H	1685		3.021	2.740	
44	4-MePh	H	1687		3.133	2.830	
45	Ph	H	1689		3.200	2.884	
46	4-BrPh	H	1690		3.243	2.918	
47	4-ClPh	H	1690		3.233	2.910	
48	3-FPh	H	1692		3.290	2.956	
49	3-ClPh	H	1692		3.302	2.966	

Table 1 - Continued

50	3-BrPh	H	1693	3.302	2.966
51	3-NO_2Ph	H	1694	3.366	3.017
52	4-NO_2Ph	H	1695	3.395	3.040
53	4-OMePh	s-cis-CH=CHPh	1666	2.123	2.019
54	4-MePh	s-cis-CH=CHPh	1668	2.235	2.109
55	Ph	s-cis-CH=CHPh	1669	2.302	2.163
56	4-ClPh	s-cis-CH=CHPh	1669	2.335	2.189
57	4-BrPh	s-cis-CH=CHPh	1669	2.345	2.197
58	3-ClPh	s-cis-CH=CHPh	1670	2.404	2.244
59	3-BrPh	s-cis-CH=CHPh	1670	2.404	2.244
60	3-NO_2Ph	s-cis-CH=CHPh	1671	2.468	2.296
61	4-NO_2Ph	s-cis-CH=CHPh	1672	2.497	2.319
62	4-OMePh	s-trans-CH=CHPh	1643	1.454	1.482
63	4-MePh	s-trans-CH=CHPh	1645	1.566	1.571
64	Ph	s-trans-CH=CHPh	1646	1.633	1.625
65	4-ClPh	s-trans-CH=CHPh	1647	1.666	1.652
66	4-BrPh	s-trans-CH=CHPh	1647	1.676	1.660
67	3-ClPh	s-trans-CH=CHPh	1647	1.735	1.707
68	3-BrPh	s-trans-CH=CHPh	1648	1.735	1.707
69	3-NO_2Ph	s-trans-CH=CHPh	1650	1.799	1.759

[a] Abbrevations: Ph - phenyl, Me - methyl, Et - ethyl, Pr - propyl

[b] Measured in CCl_4 by the technique reported in Ref 7 and given in cm^{-1}; values for compounds 43-52 taken from Ref 5; values for compounds 53-69 taken from Ref 7. The preparation and purification of compounds 1-42, used in measurements were described in Refs 9, 11-13.

[c] Not included into correlations.

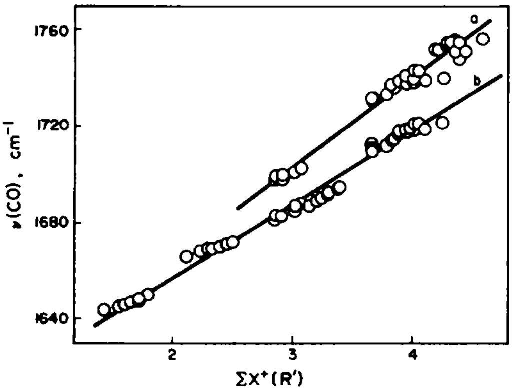


Fig. 1. Plot of the C=O stretching frequencies vs $\Sigma X^+(R')$ values for 5-phenyl-2-furancarbonyl compounds: a, O–O-*cis* conformers (II); b, O–O-*trans* conformers (I).

frequencies of these compounds are in all cases significantly higher than expected according to the eqn (2). The cause of this may be explained probably as an intramolecular H-bonding between the H atom of OH group and the O atom of furan ring.

Using the improved SPVDE[2] (valid for R_1COR_2 compounds, series III) we can determine the transmissive factors for the furan ring (more exactly, for 2,5-furylene bridge) in both O–O-*trans* a O–O-*cis* conformations as follows:

$$\tilde{\pi}(\text{Fu})_{\text{O–O-}trans} = \rho_I/\rho_{III} = 0{\cdot}803 \pm 0{\cdot}026 \qquad (4)$$

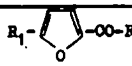
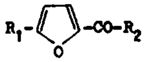
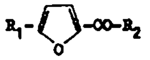
and

$$\tilde{\pi}(\text{Fu})_{\text{O–O-}cis} = \rho_{II}/\rho_{III} = 0{\cdot}979 \pm 0{\cdot}032 \qquad (5)$$

where ρ_I, ρ_{II} and ρ_{III} are the slopes of the corresponding linear correlations in series I, II and III respectively.

It follows from the eqns (4) and (5), that the transmissive factors for the furan ring in O–O-*trans* and O–O-*cis* conformations were determined with an accuracy of 3·2 and 3·3% respectively. The results show that the use of this method in determination of transmissive factors for the furan ring lead to a more accurate values, that the earlier described determinations[3-8] [$\tilde{\pi}$(Fu) was determined with an accuracy of 11–20%). It can be also confirmed that the transmissive ability of the furan ring determined in O–O-*cis* conformation is anomalously higher than in the O–O-*trans* conformation. We believe that it may be caused by different mechanism of transmission of polar effects in O–O-*cis* and O–O-*trans* conformations: Namely, in the case of O–O-*cis* conformers (II) the substituent effects are transmitted probably not only by the bonding system, but also directly by the field, which operate between the O atom of the furan ring and the CO group.

Table 2. Statistical treatment of linear correlations

Series	Compounds	Conformation	Correlation	n[a]	r[b]	ρ[c]	q[d]	s_ρ[e]	s_q[f]	s[g]
I		O–O-trans	$\nu(CO)$ vs $\sum X^+(R')$	54	0.994	30.684	1595.433	0.480	10.746	2.855
II		O–O-cis	$\nu(CO)$ vs $\sum X^+(R')$	42	0.986	37.421	1591.333	0.989	24.701	3.204
III	R_1–CO–R_2		$\nu(CO)$ vs $\sum X^+(R)$	439	0.995	38.219	1583.426	0.185	12.694	2.998
IV		O–O-trans and O–O-cis	$\nu(CO)$ vs $\sum X^+(R)$	96	0.996	38.229	1583.391	0.361	11.668	2.980

[a] Number of points used in correlation.
[b] Correlation coefficient.
[c] Slope.
[d] Intercept.
[e] Standard deviation of ρ.
[f] Standard deviation of q.
[g] Standard deviation.

Comparing the SPVDE[2] with eqns (2) and (3) respectively, it is possible to calculate the original $\Sigma X^+(R)$ values of O–O-*trans* and O–O-*cis* conformers of 5-phenyl-2-furancarbonyl compounds according to the relation:

$$\sum X^+(R) = \bar{\pi}(Fu) \sum X^+(R') + z \qquad (6)$$

where $\bar{\pi}(Fu)$ is 0·803 and 0·979 and z is 0·314 and 0·207 for O–O-*trans* and O–O-*cis* conformers respectively. The $\Sigma X^+(R)$ values calculated for all 96 O–O-*trans* and O–O-*cis* conformers of 5-phenyl-2-furancarbonyl compounds are listed in Table 1. The statistical treatment of linear correlation of corresponding C=O stretching frequencies with these calculated $\Sigma X^+(R)$ values (series IV) is given in Table 2. The comparison of data in this table shows that the regression parameters of correlations in series III and IV are practically not different. Thus, it can be concluded that similarly as in the case of $R_1CH{=}CHCOR_2$ compounds investigated before,[1] also here in the case of 5-phenyl-2-furancarbonyl compounds the C=O stretching frequencies of both conformers fit the improved SPVDE well.

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