TRANSMISSION OF THE ELECTRONIC EFFECTS OF SUBSTITUENTS BY THE THIOPHENE RING

L. P. Pivovarevich, L. A. Kutulya,
Yu. N. Surov, S. V. Tsukerman,
and V. F. Lavrushin

UDC 543.422.4:547.732.04

The shifts in the frequencies of the stretching vibrations of the hydroxyl group of phenol and pentachlorophenol that arise during the formation of hydrogen bonds with a number of substituted acetophenones and 2-acetylthiophenes, 2-acetylfuran, and 2-acetylselenophene and the frequencies of the stretching vibrations of the carbonyl group of the latter were subjected to a correlation analysis (with the Hammett, Brown, Taft, Yukawa–Tsuno, and Swain–Lupton equations), and it was shown that the thiophene ring in the investigated molecules in both the static state and during the formation of H complexes transmits the conjugation effects better than the benzene ring.

The problem of the transmission of electronic effects by five-membered heterocyclic systems – furan, thiophene, and selenophene – has recently been attracting a great deal of attention [1, 4]. As far as the thiophene ring is concerned, the information on its conductivity is quite contradictory. Thus, for example, the investigators in [2-4] concluded that the latter transmits substituent effects better than benzene, whereas Marino [1] presents contradictory data. We have previously investigated the proton-acceptor capacity of 2-acetylthiophene derivatives and some of its analogs in aqueous sulfuric acid solution [5, 6] and showed that the thiophene system is a better conductor of electronic substituent effects, particularly direct polar conjugation, than the benzene ring. It was of interest to ascertain whether this principle is characteristic only for protonation of hetetoaromatic methyl ketones in strongly acidic media or whether it also holds for other processes in which they participate. This compelled us to investigate the proton-acceptor capacity of substituted acetophenones and 2-acetylthiophenes (see Table 1) during the formation of H complexes with phenol and a more acidic proton donor – pentachlorophenol. For the characteristics of the hydrogen bond we used the shifts in the frequencies of the stretching vibrations of the hydroxyl group of the indicated proton-donor compounds ($\Delta\nu_{OH}$) that occur during interaction with the carbonyl group of the methyl ketones. In addition, we measured the frequencies of the stretching vibrations of the carbonyl group (ν_{CO}) of the investigated compounds in carbon tetrachloride solutions in order to obtain information regarding transmission of the electronic substituent effects in the benzene and thiophene systems in the static state.

The experimental data are presented in Table 1. The $\Delta\nu_{OH}$ values obtained for the H complexes of ketones with pentachlorophenol are substantially larger than for the corresponding complexes of phenol; this is a consequence of the formation of a stronger bonds when a more acidic proton donor is used [10].

It is apparent from Table 1 that when the benzene ring in acetophenone is replaced by a selenophene or furan ring the $\Delta\nu_{OH}$ values of the H complexes, which characterize their strengths, increase (compare I, XXII, and XXIII), while the $\Delta\nu_{OH}$ values for 2-acetylthiophene (XI) differ only slightly from the values for acetophenone (I). It follows from this that the electron-donor effect of the investigated hetaryl compounds increases in the order: phenyl ≈ thienyl < selenienyl < furyl. The same dependence was noted previously in an investigation of the hydrogen bonds of α,β-unsaturated ketones containing these groupings [10].

A. M. Gor'kii Kharkov State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 918-923, July 1974. Original article submitted July 10, 1973.

TABLE 1. Data from the IR Spectra of Heteroaromatic Methyl Ketones and Their H Complexes with Phenol and Pentachlorophenol

No.	Compound	$\Delta\nu_{OH}^{phenol}$, cm^{-1}	$\Delta\nu_{OH}^{PCP*}$, cm^{-1}	ν_{CO}, cm^{-1}
I	$C_6H_5COCH_3$	197	261	1691,1 †
II	$4\text{-}CH_3C_6H_4COCH_3$	207	279	1687,4 †
III	$4\text{-}C(CH_3)_3C_6H_4COCH_3$	214	283	—
IV	$4\text{-}C_6H_5C_6H_4COCH_3$	197	262	1688,3 †
V	$4\text{-}CH_3OC_6H_4COCH_3$	220	314	1683,1 †
VI	$4\text{-}C_2H_5OC_6H_4COCH_3$	220	313	—
VII	$4\text{-}ClC_6H_4COCH_3$	176	236	1691,8 †
VIII	$4\text{-}BrC_6H_4COCH_3$	177	249	1693,2 †
IX	$4\text{-}NO_2C_6H_4COCH_3$	138	—	1700,5 †
X	$3\text{-}NO_2C_6H_4COCH_3$	143	—	1700,7 †
XI	$C_4H_3SCOCH_3$	196	264	1672,2 ‡
XII	$5\text{-}CH_3C_4H_2SCOCH_3$	208	270	1668,0
XIII	$5\text{-}C_2H_5C_4H_2SCOCH_3$	210	291	1666,0
XIV	$5\text{-}CH_3OC_4H_2SCOCH_3$	232	337	1660,0
XV	$5\text{-}C_6H_5C_4H_2SCOCH_3$	203	289	1669,0
XVI	$5\text{-}ClC_4H_2SCOCH_3$	186	250	1683,0
XVII	$5\text{-}BrC_4H_2SCOCH_3$	183	232	1675,0
XVIII	$4\text{-}BrC_4H_2SCOCH_3$	174	236	1678,0
XIX	$5\text{-}IC_4H_2SCOCH_3$	182	253	1675,0
XX	$5\text{-}NO_2C_4H_2SCOCH_3$	125	—	1688,0
XXI	$4\text{-}NO_2C_4H_2SCOCH_3$	114	—	1687,0
XXII	$C_4H_3OCOCH_3$	214	285	1687,5 ‡
XXIII	$C_4H_3SeCOCH_3$	201	273	1666,0

---

*A value of 3592 cm^{-1} was assumed for ν_{OH} of the free hydroxyl group of pentachlorophenol (PCP) in conformity with [7].

† The ν_{CO} values were taken from [8].

‡ The ν_{CO} values were taken from [9].

In an investigation of the frequencies of the stretching vibrations of the carbonyl groups of methyl ketones, the heterocyclic groupings are arranged in a different sequence with respect to their effect than that noted for the $\Delta\nu_{OH}$ values: phenyl < furyl < thienyl < selenienyl. However, this is in agreement with analogous data for heterocyclic analogs of chalcones [10]. This is apparently associated with the fact that other factors, for example, the reduced mass, differences in conformation [11-14], etc., in addition to the electronic effects of the groups affect the ν_{CO} values of methyl ketones; attention was drawn to this in [15].

The effect of various substituents in the acetophenones and 2-acetylthiophenes on the spectroscopic characteristics of the investigated compounds and the H complexes corresponds to their electronic nature: electron-donor substituents increase the proton-acceptor capacity of ketones during the formation of hydrogen bonds and lower the ν_{CO} values, while electron-acceptor substituents bring about an increase in the ν_{CO} values and a decrease in the $\Delta\nu_{OH}$ values. The somewhat anomalous behavior of nitro derivatives of 2-acetylthiophene in the reaction to form H complexes with phenol was previously discussed in [16].

In order to evaluate the effectiveness of the transmission of electronic substituent effects by thiophene and benzene rings, we performed a correlation analysis of the Hammett, Brown, and Taft equations [17] and also of the two-parameter equations of the Yukawa–Tsuno [17] and Swain–Lupton [18] type. The results obtained are presented in Tables 2 and 3.

It is apparent from Table 2 that the $\Delta\nu_{OH}$ values of phenol in the series of acetophenones correlate best of all with the Hammett σ constants ($k = 0.995$). The substituent effect in this system is probably transmitted primarily via an induction mechanism; this is confirmed by the good correlation with the σ^0 parameters ($k = 0.983$). The correlation coefficient with the σ^+ parameters is highest for 2-acetylthiophenes, and effects of direct polar conjugation of the substituents with the reaction center consequently play a large role in this case, while the σ^0 values poorly characterize the effect of substituents on the reactivity of thiophene derivatives ($k = 0.909$).

The reaction constants (m), which characterize the sensitivity of the systems to the electronic effects of substituents (Hammett and Brown equations) during correlation of $\Delta\nu_{OH}$ of phenol are practically identical for acetophenone and 2-acetylthiophene derivatives; thus differences in the transmission of the electronic effects by benzene and thiophene rings are not manifested in this case.

In the series of H complexes with pentachlorophenol, the correlation coefficients are lower with respect to the one-parameter equations than in the preceding series; this is apparently associated with the

TABLE 2. Data from Correlation Analysis with Respect to the Hammett, Brown, and Taft Equations

Equation $y = ax + b$	Acetophenones				Equation $y = ax + b$	2-Acetylthiophenes			
	k*	s_a*	s_b*	n*		k	s_a*	s_b*	n
$\Delta\nu_{CO} = 16{,}13\sigma + 2{,}17$	0,978	1,21	0,45	10	$\nu_{CO} = 24{,}02\sigma + 1670{,}3$	0,967	0,97	2,53	11
$\Delta\nu_{CO} = 10{,}48\sigma^+ + 0{,}17$	0,983	0,70	0,44	10	$\nu_{CO} = 18{,}51\sigma^+ + 1673{,}5$	0,953	1,21	2,87	11
$\nu_{CO} = 16{,}08\sigma^0 + 1688{,}1$	0,922	1,20	3,00	10	$\nu_{CO} = 22{,}75\sigma^0 + 1669{,}8$	0,918	1,40	3,36	11
$\Delta\nu_{OH}P = -78{,}2\sigma + 197$	0,995	2,74	0,70	10	$\Delta\nu_{OH}P = -78{,}1\sigma + 201{,}0$	0,957	3,35	1,80	11
$\Delta\nu_{OH}P = -56{,}3\sigma^+ + 186$	0,974	5,00	0,63	10	$\Delta\nu_{OH}P = -52{,}4\sigma^+ + 193{,}0$	0,987	2,37	0,50	11
$\Delta\nu_{OH}P = -73{,}9\sigma^0 + 201$	0,983	5,06	2,90	10	$\Delta\nu_{OH}P = -82{,}0\sigma^0 + 205{,}0$	0,909	7,40	1,70	11
$\Delta\nu_{OH}PCP = -131{,}3\sigma + 268$	0,929	4,20	21,60	8	$\Delta\nu_{OH}PCP = -138{,}0\sigma + 278{,}0$	0,900	6,10	27,50	9
$\Delta\nu_{OH}PCP = -77{,}5\sigma^+ + 255$	0,974	3,10	7,30	8	$\Delta\nu_{OH}PCP = -90{,}5\sigma^+ + 262{,}0$	0,961	3,70	10,70	9
$\Delta\nu_{OH}PCP = -130{,}1\sigma^0 + 274$	0,827	6,10	36,10	8	$\Delta\nu_{OH}PCP = -140{,}5\sigma^0 + 283{,}0$	0,842	8,20	36,80	9

---

*The abbreviations used in this table are as follows: k is the correlation coefficient, s_a and s_b are the mean square errors in parameters a and b, n is the number of points, P is phenol, and PCP is pentachlorophenol.

TABLE 3. Data from Correlation Analysis with Respect to Equations of the Yukawa – Tsuno and Swain – Lupton Type

Equation $z = c + ax + by$	Acetophenones					Equation $z = c + ax + by$	2-Acetylthiophenes				
	k*	s_c*	s_a*	s_b*	n*		k*	s_c*	s_a*	s_b*	n*
$\Delta\nu_{CO} = -1{,}29 + 7{,}87F + 17{,}54R$	0,982	0,88	1,23	1,73	10	$\nu_{CO} = 1670{,}7 + 13{,}4F + 25{,}6R$	0,875	1,86	2,99	6,09	10
$\Delta\nu_{CO} = -0{,}02 + 10{,}91\sigma^0 + 10{,}77\sigma_R^+$	0,998	0,36	0,78	1,04	9	$\nu_{CO} = 1672{,}9 + 18{,}0\sigma^0 + 14{,}6\sigma_R^+$	0,908	1,66	3,15	8,31	11
$\Delta\nu_{OH}P = 196 - 43{,}2F - 82{,}7R$	0,993	1,70	2,50	5,20	9	$\Delta\nu_{OH}P = 195 - 43{,}0F - 105{,}8R$	0,961	2,40	4,70	11,2	8
$\Delta\nu_{OH}P = 194 - 63{,}9\sigma^0 - 27{,}2\sigma_R^+$	0,975	1,60	2,90	4,90	8	$\Delta\nu_{OH}P = 194 - 59{,}5\sigma^0 - 44{,}7\sigma_R^+$	0,992	1,20	3,90	4,0	11
$\Delta\nu_{OH}PCP = 256 - 57{,}2F - 166{,}5R$	0,977	1,68	3,58	6,76	8	$\Delta\nu_{OH}PCP = 263 - 74{,}9F - 201{,}4R$	0,893	2,31	14,50	32,6	8
$\Delta\nu_{OH}PCP = 254 - 80{,}6\sigma^0 - 73{,}6\sigma_R^+$	0,959	3,10	12,50	9,60	8	$\Delta\nu_{OH}PCP = 260 - 86{,}1\sigma^0 - 97{,}7\sigma_R^+$	0,928	7,40	24,30	24,9	9

---

*The following abbreviations were used: k is the correlation coefficient, s_c, s_a, and s_b are the mean square errors of the c, a, and b parameters, n is the number of points, P is phenol, and PCP refers to pentachlorophenol.

considerable effect of steric hindrance on the formation with it of a hydrogen bond because of the presence in the ortho, ortho' positions relative to the hydroxyl group of bulky chlorine atoms. This effect is undoubtedly manifested more for 2-acetylthiophenes, which exist primarily as syn conformers [11, 19] (the carbonyl group and the ring heteroatom are situated on one side of the bond connecting them). Moreover, one cannot exclude the possibility that substituents of different electron nature have a certain effect on the conformational state of the thiophene compounds and, consequently, on the degree of steric hindrance in the H complexes. However, these circumstances should not substantially interfere with the characteristics of the relative transmissions of the benzene and thiophene systems.

Judging from the correlation coefficients, the undoubtedly great role of effects of direct polar conjugation is noticeable in the formation of the hydrogen bond of ketones with pentachlorophenol. In addition, inasmuch as pentachlorophenol forms stronger hydrogen bonds than phenol, a difference is displayed in the susceptibility to electronic effects in the benzene and thiophene rings, and this difference is particularly distinct in the correlation with the σ^+ parameters ($m_T^+ > m_B^+$) and the magnitude of the transmission factor ($\gamma = m_T^+/m_B^+ = 1.17$).

Correlation analyses with the use of the two-parameter equations of the Yukawa–Tsuno (1) [17] and Swain–Lupton (2) [18] type give the best representation of the role of the various components of the electronic substituent effects in the benzene and thiophene systems:

$$\Delta\nu_{OH} = \Delta\nu_{OH}^H + m_0\sigma^0 + m_R\sigma_R^+, \tag{1}$$

$$\Delta\nu_{OH} = \Delta\nu_{OH}^H + fF + rR, \tag{2}$$

where σ^0 are constants that characterize the inductive effect of substituted phenyl, σ_R^+ characterize the capacity of a substituent for direct polar conjugation with the reaction center, F and R are constants that characterize the so-called field and resonance effects of a substituent, m_0, m_R, f, and r are coefficients of the sensitivity to the above-indicated effects, respectively.

It is apparent from the data in Table 3 that in the series of H complexes of acetophenones with both phenol and pentachlorophenol these correlation ratios are observed quite satisfactorily, and higher correlation coefficients are obtained when Eq. (2) is used. At the same time, the use of the F and R constants for 2-acetylthiophenes gives poorer results as compared with Eq. (1). We calculated the corresponding transmission factors for the thiophene ring from the m_0, m_R, f, and r parameters obtained for the analogous benzene and thiophene series: $\gamma_0 = 0.93$ $\gamma_R = 1.64$, $\gamma_f = 1.0$, and $\gamma_r = 1.28$ for H complexes of phenol; $\gamma_0 = 1.07$, $\gamma_R = 1.33$ for the H complexes of pentachlorophenol.* These values indicate approximately identical transmission of inductive (field) effects in the benzene and thiophene systems, while conjugation effects are transmitted considerably better by the thiophene ring.

The correlation of the ν_{CO} values of 2-acetylthiophenes with respect to the Hammett and Brown equations is satisfactory, although the correlation coefficients are also lower than in the acetophenone series. The values correlate poorly with the σ^0 constants.

The application of two-parameter equations of the (1) and (2) type to the frequencies of the stretching vibrations of the carbonyl group of acetophenones gives good results ($k = 0.993$ and 0.975), but the correlations with respect to these equations are considerably worse in the series of substituted 2-acetylthiophenes. The low correlation coefficients of the ν_{CO} values of 2-acetylthiophenes as compared with the values for acetophenones are probably due to the effect on the carbonyl frequencies of thiophene derivatives of possible conformational changes when substituents are introduced. In addition, as noted in [16, 20], interaction of the substituents not only with the reaction center but also with the heteroatom occurs in the thiophene ring.

The low correlation coefficients obtained on application of equations of the (1) and (2) type to the ν_{CO} values of 2-acetylthiophenes do not make it possible to form a judgment regarding the transmission of various components of the electronic substituent effects in the static state by means of the thiophene ring. However, a comparison of the reaction constants in the Hammett and Brown equations for acetophenones and 2-acetylthiophenes undoubtedly indicates in this case also the considerably greater effective transmission of the electron effects of the substituents by the thiophene ring as compared with the benzene ring.

---

*The γ_f and γ_r values for the series of H complexes of ketones with pentachlorophenol were not calculated in view of the low magnitude of the corresponding correlation coefficients.

EXPERIMENTAL

The investigated methyl ketones were obtained and purified as described in [5, 6]. The measurements of the $\Delta\nu_{OH}$ and ν_{CO} values and the purification of carbon tetrachloride and phenol were accomplished in accordance with [10]. Technical-grade pentachlorophenol was purified by reprecipitation from alkaline solution by the addition of dilute hydrochloric acid and two recrystallizations from carbon tetrachloride to give a product with mp 191°, in agreement with the literature value [7]. The correlation analysis was performed by means of the method of least squares.

LITERATURE CITED

1. G. Marino, Khim. Geterotsikl. Soedin., 579 (1973).
2. F. Fringuelli, G. Marino, and A. Taticchi, J. Chem. Soc., Perkin Trans., 2, 158 (1972).
3. D. A. Forsyth and D. S. Noyce, Tetrahedron Lett., 3893 (1972).
4. A. Perjéssy, P. Hrčiar, R. Frimm, and Z. Fisera, Tetrahedron, 28, 3781 (1972).
5. S. V. Tsukerman, L. P. Pivovarevich, L. A. Kutulya, N. S. Pivnenko, and V. F. Lavrushin, Reakts. Sposobnost' Organ. Soedin., 9, 119 (1972).
6. L. A. Kutulya, L. P. Pivovarevich, V. G. Gordienko, S. V. Tsukerman, and V. F. Lavrushin, Reakts. Sposobnost' Organ. Soedin., 9, 1043 (1972).
7. S. M. Petrov and V. S. Pilyugin, Zh. Prirodnykh. Soedin., 15, 555 (1971).
8. C. Laurence and B. Wojtkowiak, Bull. Soc. Chim. France, 3124 (1971).
9. T. G. Traylor and J. C. Ware, J. Amer. Chem. Soc., 89, 2304 (1967).
10. S. V. Tsukerman, Doctoral Dissertation [in Russian], Rostov-on-Don (1972).
11. H. J. Streurman and H. Schenk, Rec. Trav. Chim., 89, 392 (1970).
12. Z. Arlinger, K. Dahlquist, and S. Jorsen, Acta Chem. Scand., 24, 662 (1970).
13. S. V. Tsukerman, V. D. Orlov, and V. F. Lavrushin, Zh. Strukt. Khim., 10, 263 (1969).
14. P. Z. Veracini, P. Z. Barili, and Z. Lunazzi, Mol. Phys., 24, 673 (1972).
15. N. N. Zatsepina, Yu. L. Kaminskii, and I. F. Tupitsyn, Reakts. Sposobnost' Organ. Soedin., 6, 778 (1969).
16. L. P. Pivovarevich, L. A. Kutulya, Yu. N. Surov, S. V. Tsukerman, and V. F. Lavrushin, Reakts. Sposobnost' Organ. Soedin., 10, 119 (1973).
17. V. A. Palm, Fundamentals of the Quantitative Theory of Organic Reactions [in Russian], Khimiya, Leningrad (1967).
18. C. G. Swain and E. C. Lupton, J. Amer. Chem. Soc., 90, 4323 (1968).
19. H. Lumbroso, D. M. Bertin, and P. Cagniant, Bull. Soc. Chim. France, 1720 (1970).
20. L. E. Kholodov, Reakts. Sposobnost' Organ. Soedin., 5, 246 (1968).