INVESTIGATION OF H COMPLEXES OF 2-THIENYL PHENYL KETONES BY IR SPECTROSCOPY

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The shifts of the stretching vibrations of the hydroxyl groups of phenol and pentachlorophenol during the formation of intermolecular hydrogen bonds with 2-thienyl phenyl ketones containing substituents in the benzene ring were measured. A correlation dependence between the $\Delta\Delta\nu_{OH}$ values and σ^+ substituent constants was established.

In a preceding communication [1] we described the results of an investigation of the proton-acceptor capacity of 2-thienyl phenyl ketones by UV, PMR, and IR spectroscopy. The magnitude of the shift of the frequency of the stretching vibrations of the OH group of phenol in the IR spectra, which arises during the formation of a $>C{=}O\cdots H{-}O{-}$ hydrogen bond, can be used as a measure of the strength of the bases in a series of monotypic compounds [2].

Continuing our study of the basic properties of thienyl phenyl ketones, we have measured the shift in the frequencies of the stretching vibrations of the hydroxyl groups (ν_{OH}) of phenol and pentachlorophenol in carbon tetrachloride solutions that arises as a consequence of the formation of an intermolecular hydrogen bond with monosubstituted 2-thienyl phenyl ketones.

The absorption spectra of solutions of phenol and pentachlorophenol at various 2-thienyl phenyl ketone concentrations are presented in Fig. 1. The spectra contain, in addition to the absorption band of a free hydroxyl group for phenol or the associated intramolecular hydrogen bond for pentachlorophenol as ketone is added to a solution of the proton-donor, a wider band that is shifted to lower frequencies. The half-width of this band is much greater than the half-width of the absorption band of a free hydroxyl group. When the ketone concentration in the system is increased, the intensity of the high-frequency band falls, while the intensity of the low-frequency band increases. This sort of the change in the spectrum attests to the development of a hydrogen bond between the components of the solution (the complex composition is 1 : 1 [3, 4]). The broad band is affiliated with a hydroxyl group that participates in the formation of an H complex.

One's attention is drawn to the inflection at ~3300 cm^{-1} on the contours of the $\nu_{OH...O}$ band of the H complex of pentachlorophenol with 2-thienyl phenyl ketone (Fig. 1, curve b). There are contradictory opinions in this connection in the literature. Fritzsche, who observed the asymmetry of these bands [5], considered them to be doubled and explained this fact by the presence of two types of H complexes of phenol with carbonyl bases. However, Iogansen and co-workers [6] supposed that there is only local distortion of the usual contour of the broad band that is caused by disruption of the compensation of the absorption in the region of the first overtone of the carbonyl band and also possibly due to the resonance interaction of the contiguous $\nu_{OH...O}$ and $2\nu_{C=O}$ vibrational levels.

We studied the position of the first overtone of the carbonyl group of the investigated ketone in carbon tetrachloride solution ($2\nu_{C=O}$ for 2-thienyl phenyl ketone, for example, is 3260 cm^{-1}). In the formation of the H complex of the ketone with pentachlorophenol (which is a more acidic proton donor than phenol), the $2\nu_{C=O}$ band undergoes a considerable shift and, correspondingly, the compensation of the absorption at 3300-3350 cm^{-1} is disrupted (when the spectrum is recorded with a double-beam spectrometer with iden-

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TABLE 1. IR Spectra of H Complexes of α-C_4H_3SCOR with Phenol (1) and Pentachlorophenol (2)

Compound	R	1				2			
		$\nu_{OH\cdots O}$, cm^{-1}	$\Delta\nu_{OH}$, cm^{-1}	hydrogen bond strength, kcal/mole		$\nu_{OH\cdots O}$, cm^{-1}	$\Delta\nu_{OH}$, cm^{-1}	hydrogen bond strength, kcal/mole	
				acc. to 7	acc. to 8			acc. to 7	acc. to 8
I*		3430	181±1	3,1	3,9	3350	242±2	4,2	4,7
II	4-Anisyl	3421	190±2	3,3	4,1	3328	264±1	4.6	4,9
III	4-Tolyl	3433	178±2	3,1	3,9	3350	242±2	4,2	4,7
IV	Phenyl	3439	172	3,0	3,8	—	241	4,2	4,7
V	4-Diphenylyl	3442	169±2	2,9	3,8	3359	233±1	4,0	4,6
VI	4-Chlorophenyl	3451	160±3	2,8	3,6	3365	227±3	4,0	4,5
VII	4-Bromophenyl	3453	158±2	2,7	3,6	3373	219±2	3,8	4,4
VIII	4-Nitrophenyl	—	143	2,5	3,3	—	198	3,4	4.1
IX	2-Thienyl	3443	168±2	2,9	3,8	3350	235±2	4,1	4,6

* Benzophenone.

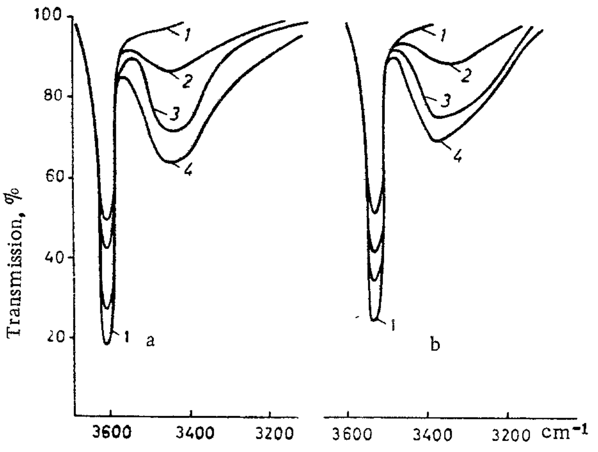

Fig. 1

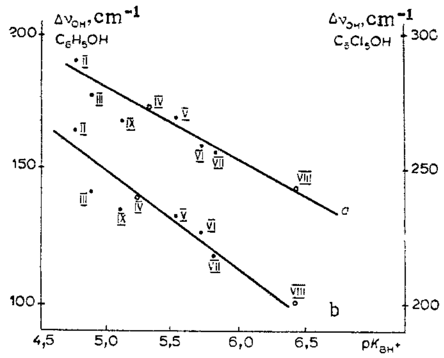

Fig. 2

Fig. 1. IR spectra of solutions of phenol (a, c = 0.01 M) and pentachlorophenol (b, c = 0.03 M) containing 2-thienyl phenyl ketone. Ketone concentration: 1) 0.00; 2) 0.01; 3) 0.05; 4) 0.10 M (a); 1) 0.00; 2) 0.05; 3) 0.10; 4) 0.15 M (b).

Fig. 2. Dependence of the pK of protolytic equilibrium and the $\Delta\nu_{OH}$ values of phenol (a) and pentachlorophenol (b) (the Roman numerals in the figure correspond to the numbers of the compounds in Table 1).

tical amounts of carbonyl compound in the paths of both beams). We therefore obtain a broad solitary absorption band of an associated hydroxyl group of the proton donor with a superimposed overtone of the carbonyl group on the base of the spectrogram (as noted by Iogansen [6]).

The shifts of the frequencies of the stretching vibrations of the hydroxyl groups of phenol and pentachlorophenol that we obtained are presented in Table 1. For comparison, the $\Delta\nu_{OH}$ values for H complexes with benzophenone are also presented in Table 1. Replacement of the phenyl ring in the benzophenone molecule by a thienyl ring is accompanied by a decrease in $\Delta\nu_{OH}$ (I and V), i.e., by a decrease in the basic properties of 2-thienyl phenyl ketone.

A similar fact was noted in the case of replacement of the benzene ring in the chalcone molecule by a thiophene ring next to the carbonyl group and was explained by the dominating effect of the negative inductive effect of the thienyl ring as compared with its positive conjugation effect [4]. In addition, the thienyl grouping creates additional steric hindrance to the approach of the phenol and pentachlorophenol molecules to the C=O group.

It is also apparent from the data in Table 1 that the $\Delta\nu_{OH}$ value is sensitive to the effect of substituents in the 4-position of the benzene ring. The introduction into the 2-thienyl phenyl ketone molecule of electron-donor substituents (II and III) leads to an increase in the $\Delta\nu_{OH}$ value, i.e., to an increase in the basicity of the compounds, while electron-acceptor substituents bring about a decrease in the electron density on the oxygen of the carbonyl group and thereby cause a decrease in the $\Delta\nu_{OH}$ values (VI and VII). Thus, the strength of the hydrogen bonds formed increases in the following order of substituents: $Br < Cl < H < C_6H_5 < CH_3 < OCH_3$. The calculated values of the hydrogen bond energy [7, 8] are presented in Table 1 and are within the limits of the values usually observed for these sorts of H complexes.

The strength of the hydrogen bonds increases in the above order of substituents when phenol is replaced by the more acidic proton-donor pentachlorophenol.

The shifts of the frequencies of the stretching vibrations of the hydroxyl groups of phenol and pentachlorophenol correlate satisfactorily (r is 0.95 for phenol and 0.97 for pentachlorophenol) with the parameters of substituents in the benzene ring in accordance with the equation $(\Delta\nu_{OH}{}^{R} - \Delta\nu_{OH}{}^{H})\,Nhc/2.303RT = \rho\sigma^{+}$, where $\Delta\nu_{OH}{}^{R}$ and $\Delta\nu_{OH}{}^{H}$ are the shifts in the frequencies of the stretching vibrations of the hydroxyl groups of phenol and pentachlorophenol with substituted and unsubstituted 2-thienyl phenyl ketones, and N, h, c, T, and R are known physical constants. The ρ values of -0.068 for phenol and -0.093 for pentachlorophenol confirm the greater polarization of the carbonyl group of ketones during the formation of a hydrogen bond with pentachlorophenol than during association with phenol. Using the linear dependence between the $\Delta\Delta\nu_{OH}$ values and σ^{+} substituent constants that we obtained, we calculated the $\Delta\nu_{OH}$ values for 2-thienyl 4-nitrophenyl ketone and for 2-thienyl 4-diphenylyl ketone, which we were unable to determine because of the insolubility of these ketones in carbon tetrachloride.

It is interesting to note the observed approximately linear dependence between the previously obtained [1] protolytic equilibrium constants and the shifts of the frequencies of the stretching vibrations of the hydroxyl groups of the proton-donor as a result of the formation of a hydrogen bond with substituted 2-thienyl phenyl ketones (Fig. 2).

EXPERIMENTAL

The 2-thienyl phenyl ketones were synthesized from thiophene and the appropriate acid chlorides via known methods [9].

The carbon tetrachloride, phenol, and pentachlorophenol were purified in accordance with known methods.

The frequencies of the stretching vibrations of the hydroxyl groups of the phenols were measured with a UR-20 spectrometer (with an LiF prism and a cuvette thickness of 4 mm for phenol and 1 mm for pentachlorophenol) in CCl_4 solutions. The phenol concentration was 0.01 M, the pentachlorophenol concentration was 0.03 M, and the ketone concentrations were 0.05 and 0.15 M, respectively. A solution of the ketone in carbon tetrachloride of the same concentration was placed in the comparison cuvette. The frequency of the stretching vibrations of the hydroxyl group of unassociated phenol was taken to be 3610 ± 1 cm^{-1}. In connection with the fact that the experimentally determined $\nu_{OH...Cl}$ band of pentachlorophenol is the band of the intramolecular hydrogen bond, the frequency of the stretching vibrations of the hydroxyl group of pentachlorophenol was taken as 3592 cm^{-1} in accordance with [10]. The position of the maximum of the band of the H complex was found by the kanod method [11]. The measurements were repeated three to five times in two independent experiments and were processed statistically with a reliability (α) of 0.95.

LITERATURE CITED

1. N. F. Pedchenko, N. D. Trusevich, N. S. Pivnenko, and V. F. Lavrushin, Zh. Organ. Khim., 8, 1882 (1972).
2. M. I. Vol'pin (editor), Modern Problems of Physical Organic Chemistry, Wiley (1972).
3. T. Gramstad, Spectr. Acta, 19, 497 (1963).
4. L. A. Kutulya, S. V. Tsukerman, Yu. N. Surov, N. S. Pivnenko, and V. F. Lavrushin, Zh. Obshch. Khim., 40, 1337 (1970).
5. H. Fritzsche, Spectr. Acta, 21, 789 (1965).
6. A. V. Ioganesen and B. V. Rassadin, Zh. Prirodnykh Soedin., 11, 182 (1969).
7. N. D. Sokolov, in: Hydrogen Bonding [in Russian], Nauka, Moscow (1964), p. 7.
8. A. V. Ioganesen and B. V. Rassadin, Zh. Prirodnykh Soedin., 11, 834 (1969).
9. H. D. Hartough, Thiophene and Its Derivatives, Interscience Publishers, New York—London (1952).
10. S. M. Petrov and V. S. Pilyugin, Zh. Prirodnykh Soedin., 15, 555 (1971).
11. S. V. Tsukerman, Yu. N. Surov, V. F. Lavrushin, and Yu. K. Yur'ev, Khim. Geterotsikl. Soedin., 868 (1966).