SPECTROSCOPIC STUDY OF ORGANOSILICON DERIVATIVES OF THIOPHENE

III.* BASICITY OF ORGANOSILICON DERIVATIVES OF THIOPHENE AND $d_\pi-p_\pi$ INTERACTION

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It is shown that the basicity of substituted thiophenes depends on the electronic effects of the substituents. The basicity of organosilicon derivatives of thiophene is determined not only by the −I effect but also by the effect of $d_\pi-p_\pi$ interaction in the Si−ring bond. The dependence of the degree of $d_\pi-p_\pi$ interaction on the nature of the three other substituents attached to the silicon atom is examined.

As we have shown by PMR spectroscopy [1,2], organosilicon derivatives of thiophene are extremely convenient subjects for a study of $d_\pi-p_\pi$ interaction. We also established the $d_\pi-p_\pi$ character of the silicon bond with the thiophene ring by IR spectroscopy [3]. The process of $d_\pi-p_\pi$ interaction is accompanied by transfer of the π-electron density of the thiophene ring to the vacant 3d orbitals of the silicon atom. A study of the effect of $d_\pi-p_\pi$ interaction on the basis of experiments that are directly associated with the magnitude of the π-electron density of the thiophene ring, i.e., with the basicity of the latter, therefore seems of considerable interest. In view of this, we undertook a study, by IR spectroscopy, of the basicity of a number of organosilicon derivatives of thiophene and some of their carbon analogs (Table 1).

The heterocyclic system of the thiophene ring has π-molecular orbitals, owing to which thiophene and its derivatives are considered to be weak π bases. In view of this, thiophene derivatives behave as electron donors during the formation of a hydrogen bond with proton donors (we used phenol as the proton donor in the present research). It is obvious that the magnitude of the electron density of the thiophene ring and, consequently, its basicity depend substantially on the nature of the substituent. The data presented in Table 1 convincingly confirm this. The $\Delta\nu$ values are the shifts in the frequency of the stretching vibration of the OH group of unassociated phenol (3609 cm^{-1}) during formation with it of an $O-H\cdots\pi$ bond with substituted thiophene. Following the point of view widely propagated in the literature [4], we assumed that the $\Delta\nu$ values are proportional to the energy of the hydrogen bond and, consequently, to the basicity of the thiophene ring. (It is known [5] that the hydrogen bond in heterocyclic aromatic systems of the thiophene, furan, and pyrrole types is formed primarily with the π electrons rather than with the heteroatom.)

We will initially consider the $\Delta\nu$ values in substituted thiophenes with methyl, chloro, and bromo groups as substituents (compounds I-IX). The introduction of a methyl group, which is a typical electron donor, into the 2 or 3 position of the thiophene ring considerably increases the basicity of the molecule – the $\Delta\nu$ values in methylthiophenes are 11-13 cm^{-1} higher than in unsubstituted thiophene. The $\Delta\nu$ values in 2,5-dimethylthiophene is 21 cm^{-1} higher than in unsubstituted thiophene, which attests to the additive contribution of both methyl groups to the increase in basicity. The introduction of a chlorine atom, which,

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*See [1] for communication II.

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TABLE 1. $\Delta\nu$ Values in the IR Spectra of the Investigated Compounds

Compound	Name	$\Delta\nu$, cm^{-1}
I	Thiophene	53
II	2-Methylthiophene	64
III	3-Methylthiophene	66
IV	2-Chlorothiophene	39
V	2,5-Dimethylthiophene	74
VI	2,5-Dichlorothiophene	26
VII	2-Bromo-5-chlorothiophene	29
VIII	2,5-Dibromothiophene	31
IX	2,3,5-Trichlorothiophene	15
X	2-Silylthiophene	44
XI	2-(Methylsilyl)thiophene	54
XII	3-(Methylsilyl)thiophene	55
XIII	Ethyldi(2-thienyl)silane	49
XIV	Tri(2-thienyl)silane	50
XV	2-(Trimethylsilyl)thiophene	63
XVI	Dimethyl di (2-thienyl)silane	59
XVII	Methyltri(2-thienyl)silane	55
XVIII	2-(Dimethylethoxysilyl)thiophene	59 (256*)
XIX	Methylethoxydi (2-thienyl)silane	65 (229*)
XX	2-(Triethoxysilyl)thiophene †	— (209*)
XXI	2-Triethoxysilyl-3-methylthiophene	73 (214*)
XXII	2,5-Disilylthiophene	40
XXIII	2,5-Di(methylsilyl)thiophene	54
XXIV	2,5-Di(dimethylsilyl)thiophene	64
XXV	2,5-Di(trimethylsilyl)thiophene	70
XXVI	2-Methyl-5-silylthiophene	57
XXVII	2-Chloro-5-silylthiophene	28

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*This is the $\Delta\nu$ value corresponding to the formation of a hydrogen bond between phenol and the oxygen atom of the ethoxy group.

† The formation of a hydrogen bond between phenol and the thiophene ring was not observed for this compound.

in contrast to the methyl group, is an electron-acceptor substituent, into the 2 position leads to a decrease in $\Delta\nu$ as compared with $\Delta\nu$ in thiophene by 14 cm^{-1}. The replacement of two and three hydrogen atoms by chlorine atoms leads to a decrease in $\Delta\nu$ of, respectively, 27 and 40 cm^{-1}. The $\Delta\nu$ value for 2,5-dibromothiophene is 22 cm^{-1} less than that for unsubstituted thiophene. The decrease in $\Delta\nu$ on passing from thiophene to 2-bromo-5-chlorothiophene is 24 cm^{-1}, which is extremely close to the sum of the additive contributions of chlorine and bromine (25 cm^{-1}). Thus both donor and acceptor substituents have an additive effect on the magnitude of the basicity of the thiophene ring as they accumulate in the molecule.

Similar dependences on the electronic effects of substituents are also observed in silyl-substituted thiophenes. Thus replacement of the methyl groups of the $Si(CH_3)_3$ fragment of (trimethylsilyl)thiophene by the more electron-accepting hydrogen atoms (transition from XV to XI and to X) leads to a decrease in the $\Delta\nu$ values. A similar decrease in the $\Delta\nu$ values also occurs when the methyl groups of 2,5-di(trimethylsilyl)thiophene are replaced by hydrogen atoms in the series of compounds XXV-XXII. Compounds containing Si−H bonds have lower basicities in the pairs of compounds XIII and XVI and XIV and XVII. The value in 2-methyl-5-silylthiophene (57 cm^{-1}) is somewhat larger than $\Delta\nu$ for unsubstituted thiophene (53 cm^{-1}). This is the result of the additive contribution of methyl and silyl substituents to the basicity of this compound. In fact, transition from thiophene to 2-silylthiophene lowers $\Delta\nu$ by 9 cm^{-1}, while transition to 2-methylthiophene raises $\Delta\nu$ by 11 cm^{-1}. As a result, the basicity of 2-methyl-5-silylthiophene exceeds the basicity of thiophene only very slightly. Similarly, the basicity of 2-chloro-5-silylthiophene is determined by the sum of the additive contributions of the electron effects of the two substituents.

A comparison of the $\Delta\nu$ values in organosilicon derivatives and their carbon analogs definitively indicates that the electronic effects of silyl substituents are the net result of the inductive effect and $d_\pi - p_\pi$ interaction. The basicities of methylthiophenes II, III and 2,5-dimethylthiophene are considerably greater than the basicities of their corresponding silicon analogs (X, XXII, and XXVI), despite the considerably higher electronegativity of the carbon atom (2.6) as compared with the silicon atom (1.9) [6]. It is also characteristic that 2-methylthiophene and 2-trimethylsilylthiophene have practically the same basicities, although the $Si(CH_3)_3$ group has a much larger +I effect ($\sigma^* = -0.9$ [7]) as compared with the methyl group ($\sigma^* = 0$). We also note that the basicities of all of the 2,5-disubstituted thiophenes that contain organosilicon substituents (XXII-XXV) are lower than the basicity of 2,5-dimethylthiophene. Starting only from higher values of the +I effect of silyl substituents as compared with the CH_3 group, one might have expected lower $\Delta\nu$ values in the carbon compounds than in the organosilicon compound.

The anomalously low basicity of organosilicon derivatives of thiophene, which cannot be explained by the inductive effect of silyl substituents, is due to the effect of the $d_\pi - p_\pi$ interaction in the silicon−ring bond. The effect of $d_\pi - p_\pi$ interaction is accompanied by transfer of π-electron density from the ring to the silicon atom. In this case the silicon atom acts as an electron-acceptor center, and the decrease in the electron density on the ring results in a decrease in its basicity.

The $\Delta\nu$ values in XVIII-XXI give information regarding the hydrogen bond not only with the ring but also with the oxygen atom of the ethoxy group. The predominant type of association with phenol in these compounds is a hydrogen bond of the $O-H\cdots O-Si$ type. However, the absorption band that corresponds to the formation of an $O-H\cdots\pi$ bond is of extremely low intensity or practically absent. The thiophene ring of 2-(dimethylethoxysilyl)thiophene has an anomalously high basicity ($\Delta\nu$ 59 cm^{-1}) as compared with that expected on the basis of only the inductive effect of three substituents attached to the silicon atom on $\Delta\nu$. In fact, the inductive effect of the ethoxy group is almost equal to the inductive effect of the three hydrogen atoms. However, 2-(dimethylethoxysilyl)thiophene has a much higher basicity than 2-silylthiophene ($\Delta\nu$ 44 cm^{-1}). This is evidence that the SiH_3 group is a greater electron acceptor than the $Si(CH_3)_2(OC_2H_5)$ fragment. The latter indicates the presence of the effect of $d_\pi-p_\pi$ interaction in the Si–O bond, which acts counter to the –I effect of the ethoxy group and therefore lowers the electron-acceptor properties of the $Si(CH_3)_2(OC_2H_5)$ fragment as a whole. In addition, the $d_\pi-p_\pi$ interaction in 2-(dimethylethoxysilyl)thiophene is apparently realized primarily in the Si–O bond. In this case, a similar interaction with the thiophene ring occurs to a small degree. Weakening of the $d_\pi-p_\pi$ bond of silicon with the ring also increases the basicity of the latter.

The $\Delta\nu$ values corresponding to a hydrogen bond between phenol and the oxygen of the alkoxy group are considerably larger than the $\Delta\nu$ values corresponding to a hydrogen bond between phenol and the ring. The reason for this is the considerably higher basicity of the oxygen atom as compared with the ring. The $\Delta\nu$ values decreased in the series of compounds XVIII-XX, which is caused by an increase in the –I effect of three substituents attached to the silicon atom. The basicity of the oxygen atom in XXI is higher than in XX owing to a decrease in the –I effect of the ring when a methyl group is introduced into it. Let us compare the $\Delta\nu$ values in XVIII and XX with $\Delta\nu$ in trimethylethoxysilane (271 cm^{-1}) and methyltriethoxysilane (237 cm^{-1}) [8]. In pairs, $(CH_3)_3SiOC_2H_5-(C_4H_3S)(CH_3)_2SiOC_2H_5$ and $CH_3Si(OC_2H_5)_3-(C_4H_3S)Si(OC_2H_5)_3$, the differences between the $\Delta\nu$ values of alkyl- and thienylethoxysilane are, respectively, 15 and 28 cm^{-1}. This indicates the greater electron-acceptor character of the thiophene ring when it enters into the composition of the 2-(triethoxysilyl)thiophene molecule. In this molecule, even the $d_\pi-p_\pi$ interaction in the Si–O bond is probably expressed to an extremely insignificant degree as compared with this sort of interaction in $(C_4H_3S)(CH_3)_2SiOC_2H_5$. This conclusion can be drawn on the basis of the data in [9] on the effects of $d_\pi-p_\pi$ interaction in alkoxysilanes. As for the $d_\pi-p_\pi$ interaction of silicon with the ring, it is apparently entirely absent in $(C_4H_3S)Si(OC_2H_5)_3$. The electron-acceptor properties of the thienyl group in this compound therefore depend only on the –I effect of this group. Owing to the large –I effect of the C_4H_3S fragment as compared with the methyl group, the basicity of the oxygen atom in 2-(triethoxysilyl)thiophene is considerably lower than in methyltriethoxysilane. In $(C_4H_3S)(CH_3)_2SiOC_2H_5$, the effect of $d_\pi-p_\pi$ interaction of silicon with the ring does occur, even though it is relatively small. This effect acts counter to the inductive effect, which can be considered as a decrease in the –I effect of the C_4H_3S group. As a result, the basicity of the oxygen atom of 2-(dimethylethoxysilyl)thiophene becomes higher than might have been expected on the basis of the inductive effect of the C_4H_3S fragment.

EXPERIMENTAL

The IR spectra of the investigated compounds were obtained with a UR-20 spectrophotometer at 3200-3600 cm^{-1}. The spectrophotometer was first thoroughly calibrated with respect to wave numbers. To measure $\Delta\nu$, a solution of phenol in carbon tetrachloride (c 0.01-0.02 M) was mixed with thiophene in volume ratios from 3:1 to 5:1. In a number of cases, a cuvette containing a solution of the thiophene in carbon tetrachloride was placed in the comparison channel of the spectrophotometer. The thickness of the absorbing layer in all cases was 4 mm.

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