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Infrared Spectroscopy of the Hydrogen Bond as a Method for the Investigation of Intramolecular Interactions

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Infrared spectroscopic data on hydrogen-bonded complexes incorporating the main classes of organic and organoelemental electron donors and electron acceptors are examined and surveyed. The dependence of the parameter $\Delta\nu$ (the frequency shift of the stretching vibration of the A-H bond in the infrared spectrum of the electron acceptor on formation of the hydrogen-bonded complex) on intramolecular interactions in the molecules of the species involved in the hydrogen bond is analysed. The use of this parameter in the investigation of weak electronic effects of substituents in the molecules of electron donors and electron acceptors involved in the formation of the hydrogen bond is considered.
The bibliography includes 191 references.

CONTENTS

I. Introduction 1198
II. Intramolecular interactions in electron donors involved in hydrogen-bonded complexes 1199
III. Intramolecular interactions in electron acceptors involved in hydrogen-bonded complexes 1206

INTRODUCTION

There has been a continuous increase in the number of reports surveying the extensive experimental data on complexes with an intermolecular hydrogen bond; these surveys help to create a modern theory of the hydrogen bond (see, for example, Refs. 1-6). At present the state of the theory is such that it permits a semiempirical (for example, on the basis of spectroscopic manifestations of the hydrogen bond) investigation of the fine details of the molecular structure of the electron acceptor A-H and the electron donor B, forming a hydrogen-bonded complex of the type A-H...B. One of the main criteria of the existence of the hydrogen bond is the shift $\Delta\nu$ of the stretching vibration frequency ν(A-H) of the electron acceptor on formation of the hydrogen bond, which can be readily measured experimentally in the infrared spectrum. The shifts $\Delta\nu$ yields important information about the structure of the electron donor and electron acceptor and particularly about the intramolecular interactions in these molecules; however, so far this information has been inadequately surveyed and analysed.

The influence of intramolecular interactions in electron donor and electron acceptor molecules on their ability to form hydrogen-bonded complexes is analysed in the present review. Among the extensive literature data, we discuss almost exclusively those obtained in the analysis of $\Delta\nu$ in infrared spectra, since these quantities are known for the majority of the hydrogen-bonded complexes investigated. Mainly studies undertaken to obtain information on the basis of the $\Delta\nu$ about the electronic structure of the species involved in the hydrogen bond (i.e. the electron donor and electron acceptor) are considered.

We shall consider briefly the validity of using the parameter $\Delta\nu$ for the solution of the problem formulated. The hypothesis[7,8] of a linear relation between $\Delta\nu$ and the enthalpy of formation of the hydrogen bond ΔH has been confirmed[9-12] only for short series of compounds. For a large number of hydrogen-bonded complexes of the type phenol (and probably any other electron acceptor) - electron donor, a quadratic relation $\Delta\nu \propto (\Delta H)^2$ is observed[3]. A relation of the type $(\Delta H)^2 = 0.11\,(\Delta\nu - 40)$ describes satisfactorily the variation of ΔH with $\Delta\nu$ over the entire known range of the energies of phenol hydrogen bonds[3], i.e. it is valid for both strong and weak hydrogen bonds. However, this relation must be used with a certain amount of caution, because it is empirical and will therefore be inevitably revised in the future as more accurate values of ΔH become available for weak hydrogen bonds. However, for the weakest hydrogen bonds $\Delta\nu$ values not only characterise the hydrogen bond but also reflect the influence of non-specific interactions in solution (for example, van der Waals interactions). However, within the limits of each of the narrow series of compounds (derivatives of benzene, ethylene, etc.) and under standard experimental conditions (constant electron acceptor, solvent, experimental temperature, and concentration, which is the case in virtually all the studies considered in this review), the influence of non-specific interactions on $\Delta\nu$ can be assumed constant to a first approximation for all the representatives of the given narrow series. The main task of the present review is a survey of the studies of intramolecular interactions in the above narrow series of electron donors on the basis of the analysis of the changes in the parameter $\Delta\nu$ in these series.

An important generalisation described in the literature is the "rule of the product of factors"[4,5], which characterises quantitatively the contributions of the electron donor and electron acceptor to the enthalpy of the hydrogen bond and, in the absence of strong steric hindrance, also in general to the capacity of the electron donor and electron acceptor for the formation of any intermolecular hydrogen-bonded complexes. This rule is characteristic of both the donor-acceptor interaction as a whole and of its special case — hydrogen bonding. It is known (see, for example, Gur'yanova et al.[13]) that the enthalpy of complex formation depends significantly on the electron densities at the donor and acceptor centres, which are in their turn determined by the intramolecular interactions (the inductive and mesomeric effects) in the donor and acceptor molecules. The influence of these effects is characterised quantitatively by the substituent constants of the Taft-Hammett type[14].

It follows that for hydrogen-bonded complexes there should be a relation between the $\Delta\nu$ and the Taft-Hammett constants of the substituents in the electron donor and electron acceptor molecules. For narrow series of electron donors, this relation should be linear. The influence of steric factors on the formation of the hydrogen bond can be estimated by methods of correlation analysis.

The great sensitivity of the parameters $\Delta\nu$ to molecular structure factors makes it possible to investigate fine details in their changes (particularly in series of compounds with related structures).

II. INTRAMOLECULAR INTERACTIONS IN ELECTRON DONORS INVOLVED IN HYDROGEN-BONDED COMPLEXES

Data for the influence of substituents linked to the donor centre, which is responsible to the greatest extent for the electron-donating capacity of the entire molecule in the formation of the hydrogen bond, were arranged systematically in the present review on the basis of the type of donor centre (an element of Group V, VI, or VII, a multiple carbon–carbon bond). Particular attention has been devoted to the consideration of intramolecular interactions in compounds containing elements of the silicon subgroup as substituents in view of the importance of this problem for the chemistry of organoelemental compounds.

1. Electron Donors containing Group V Elements

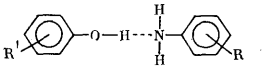
The electron-donating capacity of nitrogen derivatives R_3N varies over a wide range, and together with the inductive effect of R, is determined also by the conjugation effects in the R–N fragments and by the steric factors which control the possibility of the mutual approach of the donor and acceptor centres on formation of the hydrogen bond[10,15–22].

Table 1. The parameters $\Delta\nu$(O–H) (cm^{-1}) for the infrared spectra of certain hydrogen-bonded complexes.

Electron donor	Electron acceptor			References
	C_6H_5OH	p-ClC_6H_4OH	p-FC_6H_4OH	
H_3N	462	—	—	20
C_5H_5N	465	491	489	16
$(C_2H_5)_3N$	556	586	576	16

Table 1 shows that the frequency shift $\Delta\nu$(OH) in the hydrogen-bonded complexes of aliphatic amines and pyridine derivatives depends on the type of electron acceptor employed[16,20,23,24]. The study of hydrogen bonds between methanol and pyridine derivatives[25] showed that the presence of bulky substituents in the 2- and 6-positions in the electron donor molecule hinders the formation of the hydrogen bond. Steric factors have a similar influence both on the electron-donating capacity of pyridine derivatives in the formation of a hydrogen bond and on their basicity. This is indicated by the correlation between the parameter $\Delta\nu$(O–H) for methanol and the pK_a of pyridine derivatives. In the study of hydrogen bonds in cyclic azoles[26,27] it was established that imidazoles have a greater electron-donating capacity than pyrazoles. The electron-donating properties of the "pyridine" nitrogen atoms increase after the introduction of electron-donating substituents into the heterocycle and decrease in the presence of electron-accepting substituents.

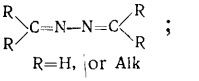
The influence of substituents in the electron donor molecule (substituted aniline) has been estimated quantitatively in relation to the hydrogen-bonded complexes between aniline and phenol derivatives[28]. The values of $\Delta\nu$(O–H) for phenol involved in the formation of a hydrogen-bonded complex of the type



are correlated with the enthalpy of complex formation and with the Hammett σ constants of the substituents R.

Elements of the nitrogen subgroup exhibit different electron-donating capacities in the formation of the hydrogen bond, decreasing in the sequence N ≫ P > As,[29,30] Such variation of the electron-donating capacities is observed also for their aliphatic derivatives. In aromatic compounds the phosphorus atom forms stronger hydrogen bonds than nitrogen[31]. Thus the values of $\Delta\nu$(O–H) for phenol are 800 and 240 cm^{-1} in the presence of $(C_2H_5)_3N$ and $(C_4H_9)_3P$ respectively and at 150 and 240 cm^{-1} in the presence of $(C_6H_5)_3N$ and $(C_6H_5)_3P$ respectively. According to the authors[31], the electron-accepting properties of tervalent phosphorus cannot be explained by the involvement of the d orbitals of the phosphorus atom in the bonding. However, we may note the appreciable discrepancy between $\Delta\nu$(O–H) obtained for triethylamine by the above workers[31] (800 cm^{-1}) and the value measured by Drago and Epley[16] (556 cm^{-1}).

The formation of multiple bonds by the nitrogen atom or its involvement in conjugation alter appreciably the electron-donating properties of compounds containing this atom as a donor centre. Thus in the azines



there may be p,π conjugation of the lone electron pairs of the nitrogen atoms with the π electrons of the neighbouring azomethine linkages[32]. The electron density at the nitrogen atoms, which determines their electron-donating properties, should therefore be determined by the degree of p,π conjugation in addition to the inductive effect of the substituents. The infrared spectra of the hydrogen-bonded complexes of azines with deuterochloroform, potentiometric data, and quantum-mechanical calculations confirmed the existence of p,π conjugation in azines[32].

The study of the electron-donating capacity of the nitriles R–C≡N and isonitriles R–N≡C established that the parameter $\Delta\nu$(OH) for phenol is correlated with the Taft inductive constant σ^* of the substituents R.[33–35] Isonitriles have a greater electron donating capacity compared with nitriles (Table 2). Thus the lone electron pair of the carbon atom in isonitriles $R-\overset{\cdot\cdot}{N}\equiv\overset{\cdot\cdot}{C}$ forms a stronger hydrogen bond than the electron pair of the nitrogen atom in nitriles. The deviations of the points corresponding to BrCN and ICN from the correlation straight line for RCN, i.e. $\Delta\nu$(O–H) = 162.7–38.56 σ^*_R, can be accounted for, according to a number of workers[33–35], by the contribution of the resonance structures $X-C\equiv N \leftrightarrow X^+ = C = N^-$. The electron-donating capacity of dimethyl aminobenzonitriles has been investigated[36]. Analysis of the correlations between $\sqrt{\Delta\nu(O-H)}$ (with phenol and methanol as electron acceptors) and the σ constants of the substituents in benzonitriles and between $\sqrt{\Delta\nu(O-H)}$ and the σ^- constants of the substituents in dimethylanilines as well as enthalpy data have shown that the nitrile group is the reaction centre in dimethylaminobenzonitriles.

Alkyl thiocyanates have a smaller electron donating capacity than nitriles[37,38] (Table 2). The values of $\Delta\nu$(O–H) for phenol involved in the formation of hydrogen bonds with alkyl thiocyanates are linearly related to the Taft σ^* constants for the alkyl substituents. On the basis of the decrease of the electron-donating capacity in the sequence nitriles > thiocyanates > isothiocyanates, it has been suggested that the hydrogen bond formed by thiocyanates involves the nitrogen atom, while that formed by isothiocyanates involves the sulphur atom[39]. The reduced electron donating capacity of the thio-derivatives compared with nitriles is associated with the conjugation within the NCS group[39]. The authors of a later study[40] of intermolecular interactions of alkyl isothiocyanates with phenol also concluded that alkyl isothiocyanates have a lower electron-donating capacity than alkyl thiocyanates and nitriles but, in contrast to Barakat et al.[39], they postulate that the hydrogen bonds of isothiocyanates are formed with the participation of the nitrogen atom and not sulphur.

Table 2. The parameters $\Delta\nu$(O–H) for the infrared spectra of hydrogen-bonded complexes (with phenol as the electron acceptor).

Electron donor	$\Delta\nu$(O–H), cm^{-1}	References
CH_3CN	159	33
$C_6H_{11}CN$	174	33
C_6H_5CN	153	33
BrCN	102	34
CH_3NC	228	33
$C_6H_{11}NC$	250	33
C_6H_5NC	203	33
CH_3SCN	146	38
C_2H_5SCN	152	38
CH_3NCS	107	40
C_2H_5NCS	113	40

A spectroscopic study of the electron-donating capacity of organosilicon amines showed[41,42] that the $\Delta\nu$(C–D) shift of the stretching frequency of the bond in deuterochloroform in mixtures with silylamines amounts to 50–60 cm^{-1} for compounds of the type $(CH_3)_3SiNHR$, 60–80 cm^{-1} for $(CH_3)_3SiNR_2$, and 30–35 cm^{-1} for the cyclic derivatives $[(CH_3)_3SiNR]_3$. In view of the greater electron-donating capacity of the isostructural carbon derivatives, the authors[41,42] concluded that there is a strong d_π–p_π interaction in the Si–N group (Table 3; compounds 1 and 2, 5 and 6, and 8 and 9). Here and henceforth in the review the d_π–p_π interaction is understood as the manifestation of the π-acceptor properties of the silicon and phosphorus subgroup elements (when these elements are linked to atoms having lone electron pairs or to α,β-unsaturated carbon substituents). Together with the hypothesis of the involvement of the vacant *nd* orbitals of these elements, there exists an alternative view concerning the explanation of the π-acceptor properties[43,44], based on an examination of hypervalent bonds[45]. The electron-donating capacities of two series of compounds, $(CH_3)_3En(CH_3)_2$ and $E[N(CH_3)_2]_4$ (E = C, Si, or Ge), have been estimated for the formation of hydrogen bonds by these derivatives with deuterochloroform[46]. The weakest hydrogen bonds are formed by silicon derivatives owing to the delocalisation of the *p* electrons of the nitrogen atom over the vacant *d* orbitals of the silicon atom (the effect of the d_π–p_π interaction). On passing to germanium derivatives the effect of the d_π–p_π interaction is appreciably weakened (Table 3; compounds 2 and 3, 6 and 7, and 9 and 10, and 11 and 12).

Table 3. The parameters $\Delta\nu$(C–D) for the infrared spectra of hydrogen-bonded complexes (with deuterochloroform as the electron acceptor).

No.	Electron donor	$\Delta\nu$(C–D), cm^{-1}	References
1	$(CH_3)_2CNHC_2H_5$	89	41
2	$(CH_3)_2SiN(C_2H_5)_2$	64	42
3	$(CH_3)_3GeN(C_2H_5)_2$	82	42
4	$(CH_3)_3SnN(C_2H_5)_2$	90	42
5	$(C_2H_5)_3N$	91	49
6	$(C_2H_5)_3SiN(CH_3)_2$	51	49
7	$(C_2H_5)_3GeN(CH_3)_2$	81	50
8	$(CH_3)_2CN(CH_3)_2$	96	46
9	$(CH_3)_3SiN(CH_3)_2$	61	46
10	$(CH_3)_3GeN(CH_3)_2$	76	46
11	$[(CH_3)_2SiNCH_3)_3$	36	48
12	$[(C_2H_5)_2GeNCH_3]_3$	77	48

Table 4. The parameters $\Delta\nu$(C–D) for the infrared spectra of hydrogen-bonded complexes (with deuterochloroform as the electron acceptor).

No.	Electron donor	$\Delta\nu$(C–D), cm^{-1}	References
1	$(C_2H_5)_3SiNC_5H_{10}$	15	54
2	$(C_2H_5)_3SiCH_2NC_5H_{10}$	60	54
3	$(C_2H_5)_2Si(CH_2)_2NC_5H_{10}$	80	54
4	$(C_2H_5)_3Si(CH_2)_3NC_5H_{10}$	70	54
5	$(CH_3)_3SiCH_2NH_2$	36	55
6	$(CH_3)_3Si(CH_2)_2NH_2$	46	55
7	$(CH_3)_3Si(CH_2)_3NH_2$	42	55
8	$(CH_3)_3Si(CH_2)_4NH_2$	43	55

The influence of molecular structure factors on the electron-donating capacity of disilazanes[47], cyclosilazanes and cyclogermazanes[48], ethyl(dimethylamino)germanes[50], and dialkylaminochlorogermanes[52] has been investigated. The electron donating capacity diminishes in the sequence C–N–C > Ge–N–Ge ≃ Ge–N–C > Si–N–C > Si–N–Si. The results were interpreted on the basis of a smaller contribution of the effect of the d_π – p_π interaction in the case of the Ge–N bond compared with the Si–N bond. Infrared spectroscopic data for silylamines[51] and trimethylsilyldiazomethane[53] also indicates the occurrence of d_π–p_π interaction in the Si–N bond.

The electron-donating capacity of organosilicon amines depends significantly on the distance between the silicon and nitrogen atoms[54]. The lower electron-donating capacity of methylsilylamines compared with that of the remaining alkylsilylamines (Table 4, compounds 2–4 and 5–8) is due to the intramolecular interaction of the nitrogen atom and silicon[55]. Similarly the reduced electron-donating capacity of $[(CH_3)_3SiCH_2]_2NH$ [$\Delta\nu$(C–D) = 49 cm^{-1}] compared with $(CH_3)_3SiCH_2N(Alk)H$ [$\Delta\nu$(C–D) ≃ 60 cm^{-1}] is caused, according to the authors[56], by the ($p \rightarrow d$) σ interaction.

2. Electron Donors containing Group VI Elements

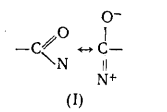
The electron-donating capacity of the oxygen atom in a wide variety of organic compounds has been studied by infrared spectroscopy[9,10,12,15,16,18,54–59,74]. It was established that the electron-donating capacity of the oxygen atom depends significantly on the nature of the substituents linked to it. In the majority of studies[12,60–62] the characteristic features of the variation in electron-donating capacity are considered solely on the basis of qualitative ideas concerning the donor-acceptor properties of substituents (see, for example, Table 7; compounds 1–6).

The formation of hydrogen bonds by a large series of ethers with different electron acceptors has been investigated[12,15]. Correlations were established between the association constant K_{ass} and $\Delta\nu$(O–H) for phenol and also between the shifts of the stretching vibration frequencies ν(X–H) of various electron acceptors for constant electron donors. The electron-donating capacity of dialkoxymethanes R′OCH$_2$OR″ has been characterised in terms of the stretching vibration frequency shift $\Delta\nu$(O–D) for deuteromethanol on formation of hydrogen bonds with the given compounds[63]. $\Delta\nu$(O–D) = 102 cm^{-1} for $(CH_3)_3COCH_2.OC(CH_3)_3$. When the t-butyl groups are replaced by the electron-accepting F_3CCH_2 groups, $\Delta\nu$(O–D) decreases to 32 cm^{-1}. The electron-donating capacity of di(β-chlorovinyl)ethers $CCl_2=CH-O-R$ depends both on the inductive effect of the substituents R and on the p,π conjugation effect. The latter leads to a decrease of $\Delta\nu$ for the given ethers compared with saturated ethers[64].

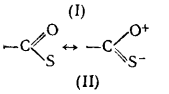
The electron-donating capacity of the carbonyl oxygen atom in the compounds $RR_iC=O$ (for constant R) decreases when R_i changes in the sequence $N(CH_3)_2 > CH_3 > OCH_3$.[65] The relation between $\Delta\nu$(O–H) and the enthalpy of formation of the hydrogen bonds between phenol and diaryl ketones $RC_6H_4COC_6H_4R'$ (where R and R′ = Cl, CH_3, H, or OCH_3) has been investigated; an increase of $\Delta\nu$(OH) for phenol following the enhancement of the electron-donating properties of the substituents R and R′ was noted[67]. The hydrogen bond involving triphenylalkylidenephosphoranes has been investigated[68,69]. As for ketones, the replacement of the methyl group in $(C_6H_5)_3P=CH-C(O)CH_3$ by the methoxy-group reduces $\Delta\nu$(O–H) for phenol; this is caused by the predominance of the *-I* effect of the methoxy-group over the mesomeric effect[69]. The very strong hydrogen bonds with phenol [$\Delta\nu$(O–H) ≃ 400 cm^{-1}] formed by these compounds have been explained[68] by the delocalisation of the charge:

$$(C_6H_5)_3P=CH-\underset{\underset{O}{\|}}{C}-R \leftrightarrow (C_6H_5)_3\overset{+}{P}-\overline{C}H-\underset{\underset{O}{\|}}{C}-R \leftrightarrow (C_6H_5)_3\overset{+}{P}-CH=\underset{\underset{O^-}{|}}{C}-R \quad .$$

The electron-donating capacity of thioesters in the formation of hydrogen bonds with phenylacetylene has also been estimated[66]. Comparison of the results with data for esters and amides showed that the electron-donating capacity of the carbonyl oxygen atom decreases in the sequence amides > esters > thioesters. This can be associated with the fact that structure (I) makes an appreciable contribution to the structure of amides, while structure (II) is significant in thioesters[66]:



(I)



(II)

The electron-donating capacities of cyclic ethers[70], ketones[71], lactones[72], and lactams[73,74] have been studied in a number of investigations. The influence of ring size is reflected in different ways in the electron-donating capacity of the oxygen atom incorporated in the ring or outside the ring. The difference has been explained[70] by the preferential formation of a hydrogen bond with the carbonyl oxygen atom and not with the oxygen atom of the alkoxy-group. However, a spectroscopic study of the hydrogen bonds between esters and trifluoroacetic acid led to the conclusion[75] that both carbonyl and alkoxy-oxygen atoms behave as electron donors.

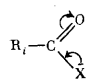
In the above investigations the principal characteristics of the changes in the electron-donating capacity of the oxygen atom in different compounds were interpreted on the basis of qualitative ideas concerning the donor–acceptor properties of the substituents. The details of the changes in the electron-donating capacity, caused by varying the substituents, frequently remained uninvestigated. Studies were therefore undertaken[76,77] to investigate the influence of the inductive and mesomeric effect of the substituents R_i on the electron-donating capacity in relation to compounds of the type R_i-O-R_i and $(R_i)_2C=O$. The influence of substituents on the electron-donating capacity of the compounds can be characterised quantitatively by the Hammett–Taft σ constants, which are known for the majority of organic substituents†.

For the compounds $(R_i)_2C=O$, where the substituents R_i exert only an inductive influence on the electron-donating capacity, the following equation was fitted by the method of least squares:

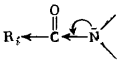
$$\Delta\nu_{ind}(cm^{-1}) = -33\Sigma\sigma^* + 190, \qquad (1)$$

which relates the values of $\Delta\nu$(O–H) for phenol to the sums of the Taft inductive constants σ^* for two substituents R_i.[76] If the substituents R_i are involved in conjugation with the oxygen atom, then the experimental values ($\Delta\nu_{exp}$) differ from those calculated on the assumption of a purely inductive influence of the substituents ($\Delta\nu_{ind}$). The difference $\Delta(\Delta\nu) = \Delta\nu_{exp} - \Delta\nu_{ind}$ characterises the conjugation with the oxygen atom.

Table 5 shows that the experimental values ($\Delta\nu_{exp}$) for the majority of compounds exceed appreciably the values calculated from Eqn. (1) ($\Delta\nu_{ind}$). The reason for the difference $\Delta(\Delta\nu)$ is the p,π conjugation effect:



as a result of which the electron density at the oxygen atom increases. The contribution of this effect rises as X is varied in the series $C_6H_5 < OAlk \simeq CH=CHC_6H_5 < NAlk_2$. On the other hand, the electron-donating capacity of the amides $R_i-C(O)-NR_2$ decreases as R_i is varied in the series $CH_3 > CH_3CH_2CH_2 > CH_3CH_2 > C_6H_5 > CH_2Cl > p\text{-}NO_2C_6H_4$.[9] It has been shown[76] that, apart from the p,π conjugation effect, in amides there is yet another mesomeric effect — p,σ conjugation:



† The application of the Hammett–Taft system makes it possible to resolve the influence of electronic effects into components associated with the inductive and mesomeric effects.

Its contribution increases with the *-I* effect of the substituents R_i.

Table 5. The values of $\Delta(\Delta\nu)$ for the infrared spectra of compounds of the type $(R_i)_2C=O$.

Electron donor	$\Delta(\Delta\nu)$, cm^{-1}	Electron donor	$\Delta(\Delta\nu)$, cm^{-1}
$CH_3COC_6H_5$	+35	$C_2H_5CON(C_2H_5)_2$	+155
$C_6H_5CH=CHCOH$	+76	$CH_3CON(CH_3)_2$	+172
$C_2H_5COOC_2H_5$	+36	$ClCH_2CON(C_2H_5)_2$	+127
$C_6H_5COOC_2H_5$	+51	p-$NO_2C_6H_4CON(C_2H_5)_2$	+143
$CH_2ClCOOC_2H_5$	+38	$Cl_3CCON(CH_3)_2$	+88

Table 6. The values of $\Delta(\Delta\nu)$ for the infrared spectra of compounds of the type R_i-O-R_i.[76]

Electron donor	$\Delta(\Delta\nu)$, cm^{-1}	Electron donor	$\Delta(\Delta\nu)$, cm^{-1}
$C_6H_5OCH_3$	−38	$CH_2=CHOC_2H_5$	−63
n-$BrC_6H_4OCH_3$	−39	$CH_2=CHOCH_2CH_2Cl$	−55
$CH_2=CHOC_6H_5$	−35	$(C_2H_5)_3SiOCH_3$	−83
$C_6H_5OC_6H_5$	−32	$(CH_3)_3SiOSi(CH_3)_3$	−255
$CH_2=CHOC(CH_3)_3$	−52	$(C_2H_5)_3SiOSi(C_2H_5)_3$	−261

The influences of the inductive and mesomeric effects on the electron-donating capacity of the oxygen atom have been separated by correlation analysis, which was also carried out for the R_i-O-R_i derivatives[76,77]. For compounds with substituents R_i which are not conjugated with the oxygen atom, the values of $\Delta\nu$(O–H) are related to the sum of the Taft inductive constants σ^* for two substituents by the linear equation

$$\Delta\nu_{ind}\,(cm^{-1}) = -90\Sigma\sigma^* + 263. \qquad (2)$$

Table 6 shows that, in compounds with $O-C_6H_5$ and $O-CH=CH_2$ fragments, the values of $\Delta\nu_{exp}$ are smaller than those of $\Delta\nu_{ind}$ calculated by Eqn. (2). This is caused by the p,π conjugation effect:

$$-\ddot{O}-CH=CH_2,$$

which acts in the same direction as the *-I* effect of aryl and vinyl substituents. The electron-accepting properties of these substituents therefore become more pronounced and the electron-donating capacity of the oxygen atom in compounds containing the given substituents is weakened. Trialkylsilyl groups have an appreciable *+I* effect. However, the values of $\Delta\nu_{exp}$ for alkoxysilanes and siloxanes are comparatively small and the differences $\Delta(\Delta\nu)$ are large. The differences are caused by the effect of the $d_\pi-p_\pi$ interaction in the Si–O fragments which consist in the delocalisation of the lone electron pairs of the oxygen atom over the vacant 3*d* orbitals of the silicon atom.

Infrared spectroscopic study of the hydrogen bond makes it possible to investigate different aspects of the conjugation effects in organoelemental compounds[78]. Thus studies of the electron-donating capacities of a number of ethers, alkoxysilanes, siloxanes[10,60,62,79–82], alkoxygermanes[61,83,89], and germoxanes[84] showed convincingly that the variation of the electron-donating capacity of the above compounds cannot be accounted for solely by the inductive effects of the substituents and the difference between the electronegativities of the central atoms. A sharp reduction of the electron-donating capacity of the oxygen atom in alkoxysilanes and siloxanes compared with carbon derivatives is a consequence of the shift of the *p* electrons of the oxygen atom to the vacant 3*d* orbitals of the silicon atom (Table 7; compounds 2 and 7 and 3 and 8). The electron-donating capacity of monoethoxygermanes is greater than that of monoethoxysilanes, which is consistent with the greater $d_\pi-p_\pi$ interaction in the Si–O bond compared with Ge–O (Table 7; compounds 7 and 13 and 12 and 17). On the other hand, the values of $\Delta\nu$(N–H) for tetraethoxygermane are only slightly greater than for tetraethoxysilane (Table 7; compounds 11 and 16), which is a consequence, according to the authors[61], of the weaker π bonding to each oxygen atom compared with that in monoethoxysilane. It has been shown[84–86] that the relative electron-donating capacities of silicon, germanium, and tin derivatives vary in the following sequences:

$$SiOC > Si(OC)_2 > Si(OC)_3 > SiOSi;$$
$$GeOGe > GeOC > Ge(OC)_2 > Ge(OC)_3;$$
$$SnOSn > SnOC > Sn(OC)_2.$$

Table 7. The parameters $\Delta\nu$(N–H) for the infrared spectra of hydrogen-bonded complexes (with pyrrole as the electron acceptor).

No.	Electron acceptor	$\Delta\nu$(N–H), cm^{-1}	References
1	$C_2H_5OC_2H_5$	149	62
2	$(CH_3)_3COC_2H_5$	149	62
3	$(CH_3)_3COC(CH_3)_3$	163	62
4	$(CH_3)_2C(OC_2H_5)_2$	138	62
5	$CH_3C(OC_2H_5)_3$	107	62
6	$C(OC_2H_5)_4$	98	62
7	$(CH_3)_3SiOC_2H_5$	138	62
8	$(CH_3)_3SiOC(CH_3)_3$	125	62
9	$(CH_3)_2Si(OC_2H_5)_2$	129	62
10	$CH_3Si(OC_2H_5)_3$	114	62
11	$Si(OC_2H_5)_4$	97	62
12	$(CH_3)_3SiOSi(CH_3)_3$	72	61
13	$(CH_3)_3GeOC_2H_5$	215	61
14	$(CH_3)_2Ge(OC_2H_5)_2$	189	61
15	$CH_3Ge(OC_2H_5)_3$	151	61
16	$Ge(OC_2H_5)_4$	119	61
17	$(CH_3)_3GeOGe(CH_3)_3$	233	84

The electron-donating capacities of cyclic organosilicon compounds with Si–O bonds have also been investigated[87]. The greater values of $\Delta\nu$ for cyclotrisiloxanes compared with cyclotetrasiloxanes can apparently be explained by the more favourable conditions for the $d_\pi-p_\pi$ interaction of the lone electron pairs of the oxygen atoms with the *d* orbitals of silicon in trimers compared with tetramers. The values of $\Delta\nu$(C–D) for alkoxy- and aminoalkoxy-silanes (with deuterochloroform as the electron acceptor) diminish with increase of the number of alkoxy-groups, i.e. with the increase of the *-I* effect of the latter[88]. The study of the electron-donating capacities of trialkoxysilanes $RSi(OR')_3$ ($R' = CH_3$ or C_2H_5; R is an organic substituent) established a linear correlation between $\Delta\nu$(A–H) for phenol or pyrrole and the Taft inductive constants for the substituents R.[90] This apparently indicates a predominantly inductive mechanism of the influence of the substituents R.

The values of $\Delta\nu$(O–H) for phenol involved in the formation of a hydrogen bond with oxygen-containing organoalkynes $(CH_3)_2(CH_2 = CHC \equiv C)COSi(CH_3)_3$ and $(CH_3)_2.(CH_2 = CHC \equiv C)SiOSi(CH_3)_3$ indicate a decrease of the electron-donating capacity of the oxygen atom in the sequence C–O–C > C–O–Si > SiOSi.[96,97] The low electron donating capacity of the oxygen atoms in the Si–O and Si–O–Si fragments can be explained by the delocalisation of the electrons of the oxygen atom over the 3*d* orbitals of the silicon atom.

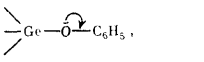
The experimental value of $\Delta\nu$(A–H) for the infrared spectrum of the electron acceptor in many instances characterises an effective electron-donating capacity of the donor in the hydrogen bond and not its true value. The difference between the true and effective values is associated with the steric hindrance of the approach of the electron acceptor molecule to the electron donor centre shielded by bulky substituents. Indeed it has been shown for alkoxy-derivatives of Group IV elements[98,99] that the t-butyl and trimethylsilyl groups give rise to steric shielding of the oxygen atom linked to them, which reduces the experimental $\Delta\nu$(A–H). Allowance for steric factors made it possible to reach a better-founded conclusion concerning the lower extent of the d_π–p_π interaction in the Ge–O bond compared with the Si–O bond.

The application of correlation analysis makes it possible to investigate fairly weak conjugation effects in alkoxy-derivatives of germanium[99]. If the substituents R in $(CH_3)_2Ge(OR)_2$ and $RGe(OC_2H_5)_3$ have only an inductive effect, then the values of $\Delta\nu$(N–H) for pyrrole and the Taft σ^* constants for these substituents are linked by the linear relations (3) and (4) respectively:

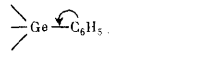
$$\Delta\nu_{N-H}(cm^{-1}) = -47\sigma_R^* + 181, \quad (3)$$

$$\Delta\nu_{N-H}(cm^{-1}) = -44\sigma_R^* + 154. \quad (4)$$

For R = C_6H_5, the corresponding points on the plots deviate from the correlation lines defined by Eqns. (3) and (4). The low values of $\Delta\nu$(N–H) for dimethyldiphenoxygermane are caused by the *p*, π conjugation effect:



and the enhanced electron-donating capacity of triethoxyphenylgermane is due to the effect of the d_π–p_π interaction in the bond, which weakens the electron-accepting properties of the phenyl group[99].



The electron-donating capacities of the organoelemental peroxides $(R_i)_3E–O–O–E'(R_i)_3$ (where E and E′ = C, Si, or Ge and R_i are alkyl or aryl substituents) depend significantly on the inductive effects of the substituents R_i linked to the E and E′ atoms[100]. If E and E′ = Si or Ge, the electron-donating capacity is also determined by the contributions of the effect of the $d_\pi - p_\pi$ interaction, which is more significant for organosilicon compounds and varies non-additively as the number of aryl substituents at the E and E′ atoms is varied.

The influence of the structure on the donor–acceptor properties of certain trialkylsilyl- and germyl-substituted alcohols has been studied[91,92] and it has been established that the electron density at the oxygen atoms in compounds with *n* > 2 in the $(CH_3)_3Si(CH_2)_nOH$ series is independent of the inductive effect of the organosilicon substituent. Evidence for the occurrence of the (*p* → *d*) σ interaction between the oxygen and silicon atoms has not been obtained. According to the values of $\Delta\nu$(O–H) found for phenol, intramolecular coordination takes place in the compounds $(CH_3)_3Si(CH_2)_nOSi(CH_3)_3$ (*n* = 1–4) when *n* = 1; for *n* ≥ 2, the effect is greatly reduced[93]. Among all the compounds investigated, the maximum value of $\Delta\nu$(O–H) was observed for $(CH_3)_3SiCH_2OSi(CH_3)_3$; nevertheless, according to the authors[93], this quantity is unduly low owing to intramolecular coordination, which partially compensates for the +*I* effect of the $(CH_3)_3SiCH_2$ group. The interpretation of the electron-donating capacities of the esters $(C_6H_5)_3ECH_2COOC_2H_5$ does not require the hypothesis of intramolecular coordination between the oxygen atom and the E atom[95]. The low value of the coordination effect and the resulting complications in its study make it at present impossible to regard the above data[91–95] as entirely correct.

The formation of hydrogen bonds by sulphur-containing compounds has been studied by a number of workers. The variation of the frequency and intensity of the ν(S–H) stretching vibration band in the infrared spectra of aliphatic mercaptans demonstrated the presence of a hydrogen bond of the type S–H... S.[101] The formation of hydrogen bonds of the type S–H... Y and X–H... S (X, Y = O, N, or S) in different classes of organic compounds has been examined in a review[102].

The electron-donating capacities of Group VI elements decrease in the sequence O > S > Se > Te. This conclusion was reached in the study of the hydrogen bonds between phenol and the compounds Alk_2X (X = O, S, Se, or Te)[59,103–106]. At the same time there is evidence for a greater electron-donating capacity of the sulphur atom compared with the oxygen atom[105]. In analysing the causes of the discrepancies between the results of these studies, one must take into account the fact that the electron-donating capacity of Group VI atoms depends significantly on the nature of the substituents linked to them[106,107]. Table 8 shows that the shift of the stretching vibration frequency ν(O–H) for phenol on formation of hydrogen bonds by the latter with the derivatives $(n\text{-}C_4H_9)_2X$ diminishes as X varies in the sequence O > S > Se > Te. The values of $\Delta\nu$(O–H) for phenol involved in hydrogen bonding with the $(C_6H_5)_2X$ derivatives diminish for different X in the opposite sequence: Se > S > O.

Table 8. The parameters $\Delta\nu$(O–H) for the infrared spectra of hydrogen-bonded complexes (with phenol as the electron acceptor).

X	$(n\text{-}C_4H_9)_2X$		$(C_6H_5)_2X$	
	$\Delta\nu$(O–H), cm^{-1}	References	$\Delta\nu$(O–H), cm^{-1}	Refs.
O	278	103	119	106
S	254	103	151	106
Se	240	103	161	106
Te	220	103	–	–

Apart from the electronegativities of the X atoms, the electron-donating capacity of $(C_6H_5)_2X$ is appreciably influenced by the *p*, π conjugation effect. The effect is a maximum for X = O, which results in a sharp decrease of the electron density at the oxygen atom in diphenyl ether and leads to the inversion of the electron capacity series

for the derivatives $(C_6H_5)_2X$ compared with $(n\text{-}C_4H_9)_2X$. Comparison of the spectroscopic and thermodynamic parameters of the hydrogen bonds between a number of electron acceptors and organic sulphides and selenides showed that the electron-donating capacity depends on the electronegativities of sulphur and selenium atoms and also on the steric and inductive effects of the substitutents[39]. The virtually identical electron-donating capacities of isostructural selenides and sulphides is a consequence of the similar electronegativities of sulphur and selenium atoms[39].

The electron-donating capacity of Group VI elements (X) changes sharply on passing from compounds with the C–X–C fragment to derivatives with the E–X–E group (where E is an element in the silicon sub-group)[42,108,109]. This is associated with the differences between the steric effects of the substituents — mainly with the sharp differences between the inductive effects and with the partial double bond character of the E–X fragments (the effect of the d_π–p_π interaction). The electron-donating capacity of Group VI elements with E = Si diminishes as X varies in the sequence Te > Se > S > O, which is exactly the opposite of the sequence of the electron-donating capacities of X in the Alk_2X derivatives[59,103,104] (see Tables 8 and 9). In series with E = Ge or Sn the maximum electron-donating capacity is shown by oxygen derivatives, but the overall sequence based on the variation of $\Delta\nu$ as a function of the nature of X also differs from the sequence of the given quantities for carbon compounds. These experiments indicate a decrease of the amount of double bond character in the E–X fragments with increase of the atomic number of the elements E and X.

Table 9. The parameters $\Delta\nu$(C–D) (cm^{-1}) for the infrared spectra of the hydrogen-bonded complexes of $[(C_2H_5)_3E]_2X$ (with deuterochloroform as the electron acceptor).[109]

X	E = Si	E = Ge	E = Sn
O	10	47	85
S	29	37	43
Se	31	42	45
Te	42	45	46

In the study of the formation of hydrogen-bonded complexes of the $R_3EXE'R_3$ and R_3EXR' derivatives (E, E' = C, Si, Ge, or Sn; X = O or S) using phenol and indole as electron acceptors the following series based on decreasing electron-donating capacities of the oxygen and sulphur atoms were obtained[110]: SnOSn > GeOGe > SnOSi > COC > SiOSi; SnSSn > GeSGe > SnSSi > CSC > SiSSi; SnOC > GeOC > SiOC; SiSC > SnSC > GeSC. It is noteworthy that the series based on the variation of the electron-donating capacity of the sulphur atom in the compounds R_3ESR' (E = Si, Ge, or Sn), found by Shevchenko et al.[110], differs from the series obtained using deuterochloroform as the electron acceptor[42]. It is known[23,24,98] that the parameter $\Delta\nu$(A–H) can depend on the type of electron acceptor employed, since the steric hindrance in the formation of the hydrogen bond is determined not only by the steric accessibility of the electron-donating centre, which depends on the structure of the electron donor molecule, but also by the dimensions of the electron acceptor molecule.

A correlation between the logarithms of the association constants and the parameter $\Delta\nu$ (A–H) for each electron acceptor was established in the systematic infrared spectroscopic study of the formation of hydrogen-bonded complexes of phosphorus-containing compounds using different electron acceptors[11,111–113]. The electron density in the P = O fragment depends on the inductive and mesomeric effects of the substituents linked to the phosphorus atom. Thus the electron-donating capacity of the oxygen atom in the vinyl-substituted organophosphorus compounds $R_2P(O).CH = CH_2$ decreases in the following sequence for different R: $N(CH_3)_2 \geqslant C_2H_5 > C_6H_5 \geqslant p\text{-}CH_3C_6H_4 > OC_2H_5 > OC_6H_5 > Cl$.[114]

The electron-donating capacities of the arsenic-containing compounds $R_3As = O$ were estimated in the study of their hydrogen bonds with phenol[115,116]. Their electron-donating capacities are much greater than those of the organophosphorus analogues. This is related particularly to the shift of electron density in the P = O fragment towards the phosphorus atom via the d_π–p_π interaction mechanism. In arsenic compounds this effect plays a smaller role.

The study of the electron-donating capacities of the derivatives $R_2S = O$ (R = Alk, AlkO, C_6H_5, or $C_6H_5CH_2$) and nitroso-compounds using phenol as the electron acceptor established a correlation between the parameter $\Delta\nu$(O–H) and the logarithms of the constants for association via hydrogen bonding[117].

It has been shown[118,119] that compounds with the fragments P = S and As = S form hydrogen bonds of the type Ph–O–H...S = X< on association with phenol. The derivatives $R_3As = S$ form stronger hydrogen bonds than the compounds $R_3P = S$, as in the case of the related oxygen-containing compounds[115,116].

Table 10. The parameters $\Delta\nu$(O–H) (cm^{-1}) for the infrared spectra of the hydrogen-bonded complexes of alkyl halides (with phenol as the electron acceptor).

R	F	Cl	Br	I
n-C_4H_9 *	40	59	69	77
n-C_7H_{15} **	40	59	69	71
cyclo-C_6H_{11} *	53	66	82	86

*Solvent–CCl_4.
**Solvent–$CCl_2 = CCl_2$.

3. Electron Donors containing Group VII Elements

The formation of intermolecular hydrogen bonds of the type O–H... Hal has been studied by a number of investigators[20,29,103,106,120,121]. Certain data[103,121] are presented in Table 10. With increase of the atomic number of the halogens, their electron donating capacity increases and

the ionisation potentials of the alkyl halides diminish[106]. The stronger hydrogen bonds formed by cyclohexyl halides compared with n-heptyl and n-butyl halides can be explained by the greater $+I$ effect of the cyclohexyl group[121], which entails an increase of the electron-donating capacity of the halogen atom.

The electron-donating capacity of the chlorine atom in $(CH_3)_3ECl$, $(CH_3)_2ECl_2$, and $(CH_3)_3ECH_2Cl$, where E = C, Si, Ge, or Sn, has been measured[122]. For the first two compounds, the electron-donating capacity of the chlorine atom increases in the sequence Si < C < Ge < Sn, which is inconsistent with the variation of the electronegativities of these elements. The anomalously low values of $\Delta\nu$(O–H) for $(CH_3)_3SiCl$ and $(CH_3)_2SiCl_2$ are related to the π-acceptor properties of the silicon atom, i.e. to the effect of the d_π–p_π interaction in the Si–Cl bond. The electron-donating capacity of the Cl atom in the compounds $(CH_3)_3$. $.ECH_2Cl$ is almost independent of the nature of the element E and can be accounted for purely by the inductive effect of the $(CH_3)_3ECH_2$ fragments. Thus the possible intramolecular coordination (σ-effect) between the chlorine atoms and E atoms (for E = Si, Ge, or Sn) was not shown under the conditions of the given experiment. Phenol used as the proton donor in the study of the hydrogen bond is fairly nucleophilic and, by solvating the organoelemental compounds at the E atom, it apparently prevents intramolecular coordination between the Cl and E atoms.

4. π-Type Electron Donors

Aromatic compounds having molecular π-orbitals form hydrogen bonds of the type O–H... π on interaction with phenols, alcohols, and other electron acceptors[123,124]. A correlation has been observed[125–127] between $\Delta\nu$(O–H) for the electron acceptor and the ionisation potentials of aromatic π-bases. The principal characteristics of the association of phenol with aromatic compounds have been studied in a number of investigations and the influence of substituents on the stability of the resulting hydrogen bonds has been examined[39,106,120,128–131,142]. The electron-donating properties of the aromatic ring are weakened as the substituents R are varied in the sequence $N(C_2H_5)_2$ > OCH_3 > Alk > C_6H_5 > CH_2Cl ~ H ~ C ≡ CH > I ~ Br > Cl > F > CF_3. The electron-accepting properties of the substituents become more pronounced in the same sequence and can be characterised by the Hammett σ_n constants. The parameter $\Delta\nu$(O–H) of phenol is virtually the same in interaction with naphthalene derivatives as in interaction with the corresponding benzene derivatives[132–134].

The possibility of an increase of the multiplicity of the E–C_6H_5, E–C = C, and E–C ≡ C (E = Si, Ge, or Sn) bonds as a result of the d_π–p_π interaction has been partly considered[43,140]. Comparison of the electron-donating capacities of silicon-containing derivatives of benzene and their carbon analogues (Table 11, compounds 3 and 15 and 4 and 16) shows that the $\Delta\nu$(O–H) of phenol in interaction with arylsilanes are lower, which indicates the operation of the effect of the d_π–p_π interaction in the Si–C_6H_5 fragment.

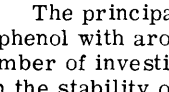
In unsaturated hydrocarbons the most weakly bound electrons are in the molecular π orbitals. Olefins are therefore classified as π-bases. The principal characteristics of the intermolecular association of olefins with phenol and p-fluorophenol have been investigated[131,133,134,135]. The electron-donating capacity of olefins increases with increase of the number of alkyl substituents attached to the sp^2-hybridised carbon atom (Table 12, compounds 1–5).

The nature of the variation of the parameter $\Delta\nu$(O–H) is in general the same as that of the ionisation potentials of the unsaturated hydrocarbons. Indeed, as alkyl substituents at a double bond accumulate, the ionisation potentials of olefins diminish; those of cyclic olefins are much lower than the ionisation potentials of their linear analogues[136,137].

Table 11. The parameters $\Delta\nu$(O–H) for the infrared spectra of the hydrogen-bonded complexes of benzene derivatives C_6H_5X (with phenol as the electron acceptor).[142]

No.	X	$\Delta\nu$(O–H), cm^{-1}	No.	X	$\Delta\nu$(O–H), cm^{-1}
1	$N(C_2H_5)_2$	83	9	H	49
2	OCH_3	62	10	I	39
3	$C(CH_3)_3$	61	11	Br	38
4	$CH(CH_3)_2$	59	12	Cl	35
5	CH_3	58	13	F	30
6	C_6H_5	52	14	CF_3	28
7	CH_2Cl	49	15	$Si(CH_3)_3$	55
8	C≡CH	49	16	$SiH(CH_3)_2$	50

Table 12. The parameters $\Delta\nu$(O–H) for the infrared spectra of hydrogen-bonded complexes (with phenol as the electron acceptor).

No.	Electron donor	$\Delta\nu$(O–H), cm^{-1}	References
1	$RCH{=}CH_2$ *	65	135
2	$RCH{=}CHR$ *	90	135
3	$R_2C{=}CH_2$ *	100	135
4	$R_2C{=}CHR$ *	110	135
5	$R_2C{=}CR_2$ *	125	135
6		108	132
7	$(CH_3)_3SiCH{=}CH_2$	56	144
8	$(CH_3)_2SiCH{=}CHCH_3$	84	144
9	$(CH_3)_2SiCH{=}C(CH_3)_2$	116	144
10	$(CH_3)_3SiCH{=}CHC_6H_5$	57	144
11	$(CH_3)_3SiCH{=}CHCl$	29	144
12	$(CH_3)_3GeCH{=}CH_2$	64	144
13	$(CH_3)_3SnCH{=}CH_2$	67	144

* R=Alk.

The above features of the influence of substituents on the electron density at a double bond also obtain for vinyl derivatives of the elements in the silicon sub-group. The increase of the number of methyl groups attached to the sp^2-hybridised carbon atom is accompanied by the additive increase of $\Delta\nu$(O–H) (Table 12, compounds 7–9). The introduction of electron-accepting substituents (the phenyl group, a hydrogen atom, and halogens; Table 12, compounds 7, 10, and 11) leads to a decrease of the π-electron density at the double bond. The electron-donating capacities of derivatives with the E–C = C fragments, where E = Si, Ge, or Sn, increase in the sequence Si < Ge < Sn (Table 12, compounds 7, 12, and 13). This sequence differs from that of the electronegativities of the elements, E, which indicates the operation of mesomeric effects in the organometallic derivatives of ethylene (d_π–p_π interaction). The effect of the d_π–p_π interaction is a maximum in silicon-containing derivatives. This also follows

from a comparison of the values of $\Delta\nu$(O–H) for vinylsilanes and related carbon compounds (see, for example, Table 12, compounds 1 and 7 and 2 and 8).

Phenol also forms hydrogen bonds with cyclopropane derivatives, which behave in many respects like compounds with a double bond[138]. For cyclopropane derivatives, the parameter $\Delta\nu$ is smaller than for alkylbenzenes and monoolefins (~40 cm^{-1}). The low electron-donating capacity of cyclopropane derivatives can probably be accounted for by the comparatively high ionisation potentials (10–9.7 eV) of these compounds[138]. On the other hand, acetylene derivatives exhibit stronger electron-donating properties compared with substituted olefins and alkylbenzenes[131,135,139]. Thus $\Delta\nu$(OH) for phenol hydrogen-bonded to butylacetylene is 90 cm^{-1}, according to West and Kraihanzel[139], and increases to 137 cm^{-1} when the second hydrogen atom is replaced by the ethyl group.

Furan and thiophen derivatives also behave as π-bases in the formation of hydrogen bonds[133,141,143]. Evidently the electron density in the furan and thiophen rings depends significantly on the nature of the substituents. The data presented in Table 13 confirm this convincingly. The introduction of methyl groups greatly increases the electron-donating capacity of furan and thiophen (Table 13; compounds 1–3 and 4–6). The substitution of hydrogen atoms by chlorine leads to a decrease of $\Delta\nu$(O–H) (Table 13; compounds 4 and 7–9). Comparison of the values of $\Delta\nu$(O–H) for organosilicon derivatives and their carbon analogues shows that the electronic effects of the silyl substituents are made up of the inductive effect and effect of the d_π–p_π interaction in the Si–thienyl bond (Table 13; compounds 5 and 10, 6 and 11, and 6 and 12).

Table 13. The parameters $\Delta\nu$(O–H) for the infrared spectra of hydrogen-bonded complexes (with phenol as the electron acceptor).

No.	Electron donor	$\Delta\nu_{O-H}$, cm^{-1}	References
1	Furan	48	133
2	2-Methylfuran	66	133
3	2,5-Dimethylfuran	82	133
4	Thiophen	52	133
5	2-Methylthiophen	64	133
6	2,5-Dimethylthiophen	74	133
7	2-Chlorothiophen	39	143
8	2,5-Dichlorothiophen	26	143
9	2,3,5-Trichlorothiophen	15	143
10	2-Silylthiophen	44	143
11	2,5-Disilylthiophen	40	143
12	2-Methyl-5-silylthiophen	57	143

III. INTRAMOLECULAR INTERACTIONS IN ELECTRON ACCEPTORS INVOLVED IN HYDROGEN-BONDED COMPLEXES

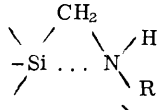
The ability of the hydrogen atom in the AH fragment to form a hydrogen bond of the type AH...X depends both on the type of electron donor X and on the nature of the atom A. If A is a carbon atom, the formation of a hydrogen bond is accompanied by only a slight change in the stretching vibration frequency $\Delta\nu$(C–H)[145–151]. Alkyne derivatives are self-associated via hydrogen bonds with participation of the ≡CH group and the π-electron cloud of the triple bond; self-association leads to a shift of ν(≡CH) by ~10–15 cm^{-1} for alkylacetylenes and ~22 cm^{-1} for phenylacetylene. The change in the stretching vibration frequency of phenylacetylene $\Delta\nu$(≡CH) can be conveniently used as a measure of the electron-donating capacity of carbonyl compounds[66,152]. The electron-accepting capacity of acetylene derivatives has also been studied using *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, and ether as bases[139,153]. The introduction of electronegative substituents leads to an enhancement of the electron-accepting capacity of the carbon atom of the ≡CH group. Thus, when the n-butyl group is replaced by the phenyl group, $\Delta\nu$(≡CH) in dimethylacetamide increases from 74 to 91 cm^{-1}.[139] The study of the infrared spectra of alkyne derivatives of the type $R_3EC\equiv CH$ (E is a Group IVB element) in electron-donating solvents showed that silicon and tin compounds form more stable hydrogen-bonded complexes than carbon derivatives[154,155,157]. This is caused by the intramolecular interaction between the π electrons of the triple bond and the vacant *d* orbitals of the elements of the silicon subgroup. Data for the electron-accepting capacity show that the above interaction diminishes with increase of the atomic number of the element of the silicon subgroup. It has been shown for organosilicon derivatives[156] that the electron-accepting properties of the $\equiv CH$ fragment in $R_3Si-C\equiv CH$ depend on the nature of the substituents R. Electron-accepting substituents at the silicon atom increase and electron-donating substituents decrease the mobility of the hydrogen atom and hence the shift $\Delta\nu$(≡CH).

Table 14. The parameters $\Delta\nu$(N–H) for the infrared spectra of hydrogen-bonded complexes (with tetrahydrofuran as the electron donor).

No.	Electron acceptor	$\Delta\nu_{N-H}$, cm^{-1}	References
1	Alk_2NH	~20	5
2	$(C_6H_5)_2NH$	94	15
3	C_4H_4NH (pyrrole)	147	15
4	$AlkNHC(O)CH_3$	~100	5
5	$CH_3NHC(O)OCH_3$	139	163
6	$C_6H_5NHC(O)OCH_3$	153	163
7	$[(CH_3)_3Si]_2NH$	71	162
8	$[(CH_2{=}CH)(CH_3)_2]_2NH$	75	47
9	$C_6H_5(CH_3)_2SiNHSi(CH_3)_3$	76	47
10	$[(CH_3)_2HSi]_2NH$	82	162

We shall now examine data for the electron-accepting capacities of compounds with the NH fragment. Primary amines exhibit a weak electron-accepting capacity. Therefore, in the study of the stretching vibration frequencies of the NH group (ν^s and ν^{as}) in aniline derivatives in electron-donating solvents (acetone, ether, and pyridine), the infrared spectra revealed comparatively small values of the parameter $\Delta\nu$(N–H).[158–161] Thus the ν^{as}(N–H) stretching vibration band in the spectrum of *p*-chloroaniline in acetone undergoes a bathochromic shift by 25 cm^{-1}. If the nitrogen atom forms part of a heterocyclic system, the parameter $\Delta\nu$(N–H) increases (Table 14; compounds 1–3). Therefore pyrrole has been used particularly widely as an electron acceptor in the study of the electron-donating capacities of organic compounds[15,57,61,85].

Table 14 shows that the electron-accepting capacity of the hydrogen atom in the NH fragment depends very significantly on the nature of the two substituents linked to the nitrogen atom. Following the enhancement of the electron-accepting properties of the substituents (Table 14; compounds 1–6), the values of $\Delta\nu$(N–H) increase. The parameter $\Delta\nu$(N–H) is therefore a sensitive indicator of the electronic effects of substituents and can be used in the study of fine details of the changes in these effects, for example, on passing from carbon derivatives to derivatives of silicon subgroup elements[47,48,51,162]. The electron-accepting capacity of silazanes, like that of amines, depends on the nature of the groups at the silicon atom, i.e. on the inductive effect of the silyl groups (Table 14; compounds 7–10). In contrast to alkyl groups, the electronic effects of organosilicon substituents are made up not only of the inductive effect but also of the effect of the d_π–p_π interaction in the Si–N bond. The R_3Si groups therefore become electron acceptors and the mobility of the hydrogen atom in the derivatives $(R_3Si)_2NH$ is appreciably higher than in secondary amines (Table 14; compounds 1, 7, and 10).

The values of $\Delta\nu$(N–H) are also a source of information about other weak intermolecular interactions in organoelemental compounds, for example about the α-effect.[163] The latter obtains in compounds with an $E-CH_2-X$ fragment (E is an element of the silicon subgroup or another atom having vacant orbitals and X is an atom having lone electron pairs) and represents intramolecular coordination, for example, . In amides and amines containing groups of the type $\equiv Si-CH_2-N(R)H$, the electron-accepting capacity of the hydrogen atom in the NH group depends on the electronic effects of the substituent R linked to the nitrogen atom (the I effect, p,π conjugation, and the α-effect)[163]. The α-effect depends on the nature of the substituents R. When R = Alk, the α-effect is a maximum; it decreases for R = C_6H_5 owing to competition with the effect of p,π conjugation; when R = $C(O)OCH_3$, there is no α-effect.

A large number of spectroscopic studies of the formation of hydrogen bonds with participation of OH groups and various electron donors have been made[12,15,67,96,106,164–178]. The electron-accepting capacity increases after the introduction of electron-accepting substituents into the molecule. Thus the O–H stretching vibration frequency shift $\Delta\nu$(O–H) in the infrared spectrum of tetrafluoropropanol dissolved in acetone is 165 cm^{-1}, while the corresponding shift for propanol is only 110 cm^{-1}.[67] The electron-accepting capacity of chloroalcohols increases as chlorine atoms accumulate in the molecule[168,169]. However, the electron-donating capacity of alcohols then diminishes, which induces a decrease of the degree of self-association of chloroalcohols. Thus the ν(O–H) stretching vibration band of $(CCl_3)_2CHOH$, corresponding to an associated species formed via an intermolecular hydrogen bond, is not observed even at an alcohol concentration of ~2 M.

The electron-accepting properties of phenol derivatives can be regulated over a wide range by varying the nature of the substituents in the aromatic ring[171–173]. The introduction of electron-accepting substituents in the p-position in phenol increases the mobility of the hydrogen atom of the OH group. $\Delta\nu$(O–H) for phenol in diethyl sulphide is 256 cm^{-1}, increasing to 280 cm^{-1} for p-chlorophenol[105].

The stretching vibration frequency of the S–H bond changes little on formation of a hydrogen bond. It was therefore believed for a long time that the self-association of the corresponding compounds via the formation of hydrogen bonds of the type S–H. . . S does not occur. However, subsequently the presence of hydrogen bonds of this type was demonstrated and certain characteristics of the formation of such hydrogen-bond complexes were investigated: the dependence of the electron-accepting capacity of the S–H group in p-substituted thiophenols on the nature of substituents[179]; the presence of a hydrogen bond of the type S–H. . . S in aliphatic thiols and of the type S–H. . . S and S–H. . . π in benzenethiols and α-toluenethiols[180]; the formation of a hydrogen bond between mercaptans RSH and amines, ethers, and thioethers[101]. Comparison of the electron-accepting capacities of the OH and SH groups in the formation of an intermolecular hydrogen bond showed that the hydrogen in thioacids is less mobile[181,182]. The greater shielding at the proton in the SH group is normally due to the more diffuse nature of the orbitals of the outer electrons of the sulphur atom compared with the outer orbitals of the oxygen atom[182].

Table 15. The parameters $\Delta\nu$(O–H) for the infrared spectra of hydrogen-bonded complexes (with tetrahydrofuran as the electron donor).

No.	Electron acceptor	$\Delta\nu$(O–H), cm^{-1}	References
1	$(C_6H_5)_3COH$	208	140
2	$(C_6H_5)_3SiOH$	338	140
3	$(C_6H_5)_3GeOH$	211	140
4	$(C_6H_5)_3CCH_2OH$	140	187
5	$(C_6H_5)_3SiCH_2OH$	160	187
6	$(C_6H_5)_3GeCH_2OH$	170	187
7	$(C_6H_5)_3CCH_2CH_2OH$	165	187
8	$(C_6H_5)_3SiCH_2CH_2OH$	155	187
9	$(C_6H_5)_3GeCH_2CH_2OH$	160	187
10	$(C_6H_5)_3COOH$	330	190
11	$(C_6H_5)_3SiOOH$	408	190
12	$(C_6H_5)_3GeOOH$	335	190
13	$(C_6H_5)_3SnOOH$	258	190

The formation of hydrogen-bonded complexes by organoelemental compounds of Group IVB elements was first studied[140,183–185] in relation to alcohols of the type R_3EOH and $(C_6H_5)_3EOH$, where E is an element of the silicon subgroup. Diethyl ether, mesitylene, and tetrahydrofuran were studied as electron donors. Compared with the corresponding carbinols, silanols exhibit much greater shifts $\Delta\nu$(O–H) (Table 15, compounds 1–3). The series corresponding to the diminution of the electron accepting properties of alcohols as a function of the element E(Si > Ge ≃ C > Pb ≃ Sn) does not agree with the electronegativity series of these elements. Taking into account only the inductive effect, it was to be expected that the greatest electron-accepting capacity would be shown by carbinols and germanols. On the basis of these data, it was concluded[140,183–185] that the d_π–p_π interaction takes place in the E–O fragments, its intensity diminishing as E is varied in the sequence Si > Ge > Sn > Pb. The greater electron-accepting capacity of vinylacetylenic silanols compared with their carbon analogues can also be explained by the d_π–p_π interaction between the oxygen and silicon atoms[96]. The greater electron-accepting capacity

of silanethiols compared with the corresponding thiols is due to the delocalisation of the lone electron pair of the sulphur atom over the 3*d* orbitals of the silicon atom, which increases the mobility of the hydrogen atom in the Si–S–H fragment[186].

The electron-accepting capacity of the hydrogen atom in the test compounds decreases in the sequence $(C_6H_5)_3$. .SiSH $\gg$ C_6H_5SH > $(CH_3)_3SiSH$ > $(C_6H_5)_3CSH$ > $(CH_3)_3CSH$, which is analogous to the sequence based on the decrease of the mobility of the hydrogen atom of the given group in oxygen-containing compounds: $(C_6H_5)_3SiOH \gg C_6H_5OH$ > $(CH_3)_3SiOH$ > $(C_6H_5)_3COH$.[184] In the series of alcohols $(C_6H_5)_3ECH_2OH$ the electronegativities of the Group IVB elements E suggested that the carbinol should have the greatest electron-accepting capacity. However, the experimental electron-accepting capacity series for the alcohols is different: $(C_6H_5)_3GeCH_2OH$ > $(C_6H_5)_3SiCH_2OH$ > $(C_6H_5)_3CCH_2OH$ (Table 15, compounds 4–6). This fact can probably be accounted for by an intramolecular coordination of the type $(p \rightarrow d)\sigma$ between the oxygen and germanium atoms as a result of the existence of the vacant 4*d* orbitals in the latter. In the silicon derivative this effect is less pronounced and in the carbon derivative it is altogether absent. The nature of the element E has almost no influence on the mobility of the hydrogen atom in the alcohols $(C_6H_5)_3ECH_2CH_2OH$,[187] because the inductive effect of groups $(C_6H_5)_3ECH_2CH_2$ changes only slightly as E is varied (Table 15, compounds 7–9). There is apparently no intramolecular coordination in these compounds.

In the study of the electron-accepting properties of the silicon containing alcohols $(CH_3)_3Si(CH_2)_nOH$ and $R(CH_3)_2$. .$SiCH_2OH$ (n = 1–4, R = C_2H_5 or C_6H_5) the authors[91,188] concluded that there is no intramolecular interaction in these compounds between the oxygen and silicon atoms. However, intramolecular interaction does take place in the compounds $C_6H_5(CH_3)_2Si(CH_2)nOH$ (n = 1, 2) and $(C_6H_5)_3$. .$SiCH_2OH$.[188] This interaction apparently involves the formation of an intramolecular hydrogen bond, since in the carbon analogues the effect is more marked.

When the electron-accepting capacities of organosilicon hydroperoxides, carbinols and silanols and organic hydroperoxides were compared, the following series were obtained[189]: $R_3COH < R_3SiOH$, $R_3COH < R_3COOH$, $(CH_3)_3$. .$EOH < (C_6H_5)_3EOH$ (E = C or Si); $R_3SiOH < R_3SiOOH$, $(CH_3)_3SiOOH < (C_6H_5)_3SiOOH$, $R_3COOH < R_3SiOOH$ (R = CH_3 or C_6H_5). The results indicate the operation of the effect of the d_π–p_π interaction in the Si–O bond.

The electron-accepting capacity of the hydroperoxides $(C_6H_5)_3EOOH$ (E = C, Si, Ge, or Sn) decreases in the sequence $(C_6H_5)_3SiOOH$ > $(C_6H_5)_3GeOOH$ > $(C_6H_5)_3COOH$ > $(C_6H_5)_3SnOOH$ (Table 15, compounds 10–13). This leads to an electronegativity series of Group IV elements, Si > Ge > C > Sn, which differs from the corresponding series in the absence of conjugation effects: C > Ge > Si $\approx$ Sn.[191] This discrepancy between the electronegativity series can be accounted for by the effect of the d_π–p_π interaction, which diminishes in the sequence Si > Ge > Sn.

* * *

Thus the parameter $\Delta\nu$, which can be most readily determined experimentally from the infrared spectrum, serves at the same time as a source of fairly extensive information both in a qualitative assessment of the weak effects of substituents in the molecules involved in the hydrogen bond and in a semiempirical study of the effects using the Taft–Hammett system. This method for the investigation of intramolecular interactions has been by no means exhausted in the study of organic compounds; a quantitative theory relating the parameter $\Delta\nu$ to molecular structure factors will probably be created in the future. The simplicity and clarity of the method makes it promising for the study of organoelemental compounds, where the inadequate development of the theory of chemical bonding frequently restricts the employment of complex research techniques.

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