Translated from *Uspekhi Khimii*, **46**, 602-638 (1977) U.D.C. 541.571.9

Weak Hydrogen Bonds

V.K.Pogorelyi

The literature data on the properties of hydrogen bonds involving the elements in the Third, Fourth, and Fifth Periods are surveyed and an attempt is made to determine the factors which have a decisive effect on the proton- and electron-donating capacities in series of compounds of the same type formed by elements in different Periods and Groups.
The bibliography includes 222 references.

CONTENTS

I. Introduction 316
II. The hydrogen bond involving sulphur compounds 316
III. Variation of the proton- and electron-donating capacities in series of compounds of the same type formed by Group V-VII elements 326
IV. Certain general problems of the hydrogen bond 331

I. INTRODUCTION

Hydrogen bonds play an important role in various chemical, physical, and biological reactions[1], which is the reason for the increasing interest in the study of various systems with hydrogen bonds. However, the majority of investigations have been concerned with hydrogen bonds in compounds formed by the elements in the Second Period, such as nitrogen, oxygen, fluorine, and (to a lesser extent) carbon. Extensive experimental[1-7] and theoretical[8-11] data have accumulated in this field and have been to a large extent reviewed. Hydrogen bonds involving elements in the Third and subsequent Periods have been investigated much less. The available information about this problem is sporadic and frequently contradictory. Until recently, it used to be assumed[1] that these elements either do not tend to form hydrogen bonds or give rise to relatively weak bonds.

In recent years, there has been a significant growth of interest in the so called weak† hydrogen bonds for two reasons. Firstly, the course of chemical processes is determined not only by strong interactions associated with large changes in the energy of the reactants but also by weak interactions, which influence the process probability but hardly alter the energy spectrum of the reaction. Such interactions play an especially important role not only in chemical but also in biological systems. Secondly, studies of this kind extend significantly our ideas about the nature of the hydrogen bond.

This review deals with studies on weak hydrogen bonds involving the atoms of Group V–VII elements. A separate section is devoted to the properties of hydrogen bonds involving sulphur compounds, since after the publication of the review of Zuika and Bankovskii[12], the literature was supplemented by numerous quantitative data. This section includes also studies which showed that the properties of hydrogen bonds between interacting molecules determine not only the kinetics but also the mechanism of the fast proton exchange reaction. Particular attention has been devoted to the identification of the factors which determine the nature of the changes in the proton- and electron-donating capacities in the hydrogen bond as a function of the electronic structure of the relevant atoms, i.e. as a function of their position in the Periodic System.

In this paper, an attempt is made to survey and analyse the available literature data (up to 1974 inclusive) for the properties of weak hydrogen bonds and about the influence of these bonds on protolytic reactions, such as tautomerism and rapid proton exchange.

II. THE HYDROGEN BOND INVOLVING SULPHUR COMPOUNDS

1. MERCAPTANS AND THIOPHENOLS

(a) Self Association

There is no doubt about the self association which occurs in liquid mercaptans RSH and their solutions in inert solvents as a result of the SH...S hydrogen bonds. The spectroscopic and physicochemical studies on this problem have been considered in detail in a review[12]. However, the vast majority of the relevant data are qualitative. Quantitative results on the self association of mercaptans have been obtained by Miller and coworkers[13-16] using NMR. Hu and Miller[16] studied the self association of mercaptans in terms of the variation of the chemical shift of the SH protons (τ_{SH}) with concentration in carbon tetrachloride or cyclohexane solution. The measured dimerisation constants K showed that the tendency towards self association increases in the sequence $C_6H_5SH \ll C_2H_5SH <$ n-$C_3H_7SH <$ i-$C_3H_7SH <$ n-C_4H_9SH.

The hydrogen bond strengths ΔH in the self-associated species of mercaptans, aminomercaptans, and mercaptoethers have been obtained[16-24]. According to Yablonskii et al.,[21] $-\Delta H = 0.1-0.4$ kcal mole^{-1} for the SH...S hydrogen bonds and $-\Delta H = 0.5-0.8$ kcal mole^{-1} for the SH...O bonds in mercaptoethers. Hu and Miller[16] determined the SH...S bond strength in the self-associated mercaptan species from the temperature variation of τ_{SH}. As in the study of Marcus and Miller[15], relatively low values of K were obtained. It was found that the bond strength ($-\Delta H \simeq 1$ kcal mole^{-1}) is likewise low and depends little on the nature of the substituents. A low SH...S bond strength is indicated by the results of quantum-chemical calculations

† We employ the term weak for hydrogen bonds whose formation involves the elements in the Third, Fourth, and subsequent Periods.

for the hydrogen bond in H_2S solutions[25-27] ($-\Delta H \simeq 1.7$ kcal mole^{-1}). The infrared spectroscopic studies on certain mercaptans at reduced temperatures by Alencastro and Sandorfy[28] agree with these data. The tendency towards self association increases on passing to aminomercaptans.

Table 1 shows that mercaptans form weak hydrogen bonds, whose strength is much lower than that of the analogous alcohol complexes. This can be explained by the fact that, on passing from oxygen to sulphur, there is an appreciable decrease of the proton- and electron-donating capacities of the hydrogen bond (see below).

When the mercaptan molecule contains electronegative atoms such as oxygen and nitrogen (mercaptoethers and aminomercaptans), the tendency towards self association should increase, since there is an increase in the proton-donating capacity of the SH group and the possibility of the formation of the SH...O and SH...N hydrogen bonds with stronger electron donors appears.

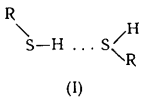
Table 1. The thermodynamic characteristics of the hydrogen bond in the dimers of certain mercaptans.

RSH	$k^{30°}$, litre mole^{-1}	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.	References
n-C_3H_7SH	0.0051	0.9	13	16
iso-C_3H_7SH	0.0050	0.8	13	16
n-C_4H_9SH	0.0035	0.8	14	16
t-C_4H_9SH	0.0014	1.1	16	16
$C_6H_{11}SH$	0.0001	0.7	15	16
HSH	—	1.7**	18	20
C_6H_5SH	—	1.2	—	17
$R_{3-n}(CH_2CH_2SH)_n^*$	—	1.9—2.5**	—	19

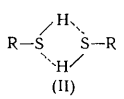
*The SH...N bond, in the remaining cases the SH...S bond.
**The infrared spectroscopic method, in the remaining cases the NMR method.

A study has been made[29] of the self association of *p*-substituted thiophenols and the interaction of the SH groups with the heteroatoms of the substituents has been observed. *p*-Amino- and *p*-fluoro-thiophenols are self-associated to a greater extent than thiophenol itself owing to the formation of the SH...N and SH...F bonds.

The structure of the self-associated thiol species constitutes at the present time the most controversial problem. With the exception of rigid systems, such as those in crystals, or systems with fixed configurations, such as those in biopolymers, it is difficult to characterise the geometry of the hydrogen bond. Since a linear hydrogen bond is usually stronger, presumably open-chain dimers (I) should be formed preferentially in solution. Indeed quantum-chemical calculations for NH_3, H_2O, H_2S, and HF have shown that type (I) dimers are energetically preferable[30-34]. However, the relatively low entropies of the hydrogen bond (Table 1) can be explained by the formation of cyclic dimers (II)[16]:



(I)



(II)

Structures (I) and (II) probably exist in solution. According to data[16,28] for aromatic thiols, apart from dimers (I) and (II) there is a possibility of complexes with the hydrogen bonds SH...π, the formation of which should lead to an additional increase in the complexity of the structure of the solution. However, the conclusion[15] that the thiophenol self-associated species have a tetrameric structure in carbon tetrachloride solution at a normal temperature is doubtful, since the infrared spectra show bands corresponding to self-associated species of a higher order than dimers only at low temperatures[28].

On the basis of the available data[16,17,35,36], one can formulate a series in terms of the decrease of the hydrogen bond strength ($-\Delta H$, kcal mole^{-1}) in the self-associated species of the alkyl compounds or hydrides of various elements:

$$ROH(\sim 4) > RNH_2(\sim 3.5) > RSH(\sim 1) \gg R_3CH$$

or

$$HF > H_2O > H_3N > H_2S \gg H_4C.$$

Evidently this series agrees with the electronegativity series for the corresponding elements.

(b) Association

The results of the study of physicochemical properties and spectroscopic investigations have shown that mercaptans and thiophenols form associated species in proton-donating solvents via the SH...O, SH...N, SH...Cl, etc. hydrogen bonds. However, there are relatively few quantitative data for the properties of these bonds and a systematic treatment of the latter is not available. The first quantitative characteristics of association involving thiophenol as the proton donor were obtained by NMR[37-39]. A detailed study of the hydrogen bonds in the 1 : 1 associated species of certain mercaptans with various electron donors has been made by Hu et al.,[40] who investigated hydrogen bonds of the type SH...S, SH...O, SH...O=C, SH...O=S, SH...O=P, and SH...N. It was found that the strengths of these bonds are low (Table 2) and change little when the electron donor is altered. For the same electron donor, the strengths of hydrogen bonds with various alkanethiols are virtually constant.

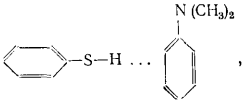
Table 2. The thermodynamic characteristics of the hydrogen bonds between certain mercaptans and different electron donors[40].

Donor	t, °C	$\Delta\tau_C$, p.p.m.	10^2K, litre mole^{-1}	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
		iso-C_3H_7SH			
$(CH_2)_4S$	32.6	1.65	3.1	0.8	9.0
$(CH_3)_2S$	32.2	0.92	3.7	0.5	8.0
$(CH_3)_2CO$	32.2	1.24	4.7	0.9	9.0
$(CH_3)_2O$	30.2	0.81	6.1	1.0	9.0
$(CH_3O)_2SO$	30.4	0.51	12.0	0.9	7.0
$(C_2H_5O)_3PO$	31.5	2.41	6.5	1.0	9.0
$[(CH_3)_2N]_3PO$	44.2	15.28	2.0	1.1	11.0
CH_3CN	31.2	0.45	13.0	0.6	6.0
$[(CH_3)_2N]_2CO$	34.9	2.22	5.9	1.1	9.0
		n-C_4H_9SH			
$(CH_3)_2SO$	34.2	0.95	17.0	0.9	6.0
$(C_2H_5O)_3PO$	34.2	1.47	12.0	1.0	8.0
		t-C_4H_9PH			
$(CH_2)_4S$	36.0	0.38	14.0	0.7	6.0
$(CH_3)_2S_2$	36.0	1.23	3.1	0.6	9.0
$(CH_3)_2CO$	35.2	0.97	6.4	0.9	8.0
$O(CH_2—CH_2)_2O$	31.9	1.06	5.5	0.6	8.0
$HCON(CH_3)_2$	36.0	1.41	8.4	0.9	8.0
$(CH_3)_2SO$	31.9	0.60	30.0	0.9	5.0
$(C_2H_5O)_3PO$	32.7	2.43	6.9	1.0	8.0

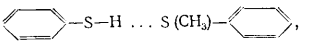
Table 2 and literature data[37,38] show that there is no correlation for the association of thiols with various electron donors between the chemical shift on complex formation $\Delta\tau_C$ and the bond strength‡. The equilibrium constant K is likewise unrelated to the bond strength[40]. Its changes for different electron donors are determined mainly by the change in entropy.

Hydrogen bonds involving thiophenol have been investigated to a somewhat greater extent. The thermodynamic characteristics of the hydrogen bonds between thiophenol and electron donors of different types have been obtained[43,44]. The association of thiophenol, thiocresol, and *p*-bromothiophenol with ethylene trithiocarbonate has been studied by ultraviolet spectroscopy[45]. The dimerisation constants obtained (K_2, litre mole^{-1}) were used to establish a series based on the variation of the proton-donating capacity of the thiophenols investigated: *p*-bromothiophenol (0.87) > *p*-thiocresol (0.75) > thiophenol (0.64). This series is inconsistent with the expected acidities of the thiophenols[46,47] (which was also noted by Mukherjee et al.[45]) and with the conclusions reached by the present author and Gragerov[39]. Possibly the discrepancies are due to the inaccuracies in the determination of K_2.

The present author and Kukhtenko[48] studied by NMR the association of thiophenol and its derivatives with electron donors of the *n*- and π-types: anisole, dimethyl-aniline, and thioanisole. The concentration and temperature variation of τ_{SH} showed that thiophenol forms mainly complexes of the π-type with dimethylaniline:



while n-complexes are mainly formed with thioanisole:



for which $-\Delta H = 1.6$ kcal mole^{-1} and $-\Delta S = 9.0$ e.u. were obtained. It was found that the probabilities of the formation of *n*- and π-complexes with anisole are almost identical. The hydrogen bond formed by thiophenol with butyl methyl ether is characterised by the following parameters: $-\Delta H = 2.7$ kcal mole^{-1} and $-\Delta S = 9.6$ e.u. Comparison of the heats of association of thiophenol with this ether and acetone showed that the ketone forms a stronger bond ($-\Delta H = 3.2$ kcal mole^{-1}).[39] This result conflicts with the view[49] that ethers should form stronger hydrogen bonds than ketones, since the lone electron pair of the oxygen atom in ketones has a greater amount of *s* character (sp^2 hybridisation). This treatment is based solely on the donor–acceptor model of the hydrogen bond and does not take into account the contribution of the electrostatic interaction, which is probably significant for ketones owing to the strong polarisation of the bond in the carbonyl group.

The data obtained[37,48] make it possible to arrange the bases investigated in a series in terms of decreasing π-electron-donating capacity in relation to the formation of hydrogen bonds with thiophenol: *NN*-dimethylaniline > anisole > benzene > thioanisole. Thioanisole is a less effective π-electron donor, since the π-electron density in its ring may be reduced owing to π–d conjugation. Furthermore, the p–π conjugation in thioanisole is less effective than, for example, in anisole itself, since the difference between the energy levels of the p and π electrons ($\Delta n = 1$) hinders the interaction of these orbitals[50]. The above hypotheses agree with the type of change in the Hammett σ constants on passing from alkoxy- to alkylthio-substituents[51].

The influence of the electronic nature of the substituents in both proton donor and electron donor molecules on the spectroscopic and thermodynamic characteristics of the SH...O=C hydrogen bond in the thiophenols–acetophenones system has been investigated[52] by NMR. As was to be expected, the stability of the associated species increases with increase of the electron-accepting capacity of the substituents in the thiophenol ring. The dependence of ΔH on the Hammett σ constants is described by the equation

$$\Delta H_A = 2.2 + 1.9\sigma. \quad (1)$$

The energy of the hydrogen bond increases with increasing electron-donating capacity of the substituent in the acetophenone molecule:

$$-\Delta H_B = 2.4 - 1.2\sigma. \quad (2)$$

Comparison of the reaction constants for the two series investigated ($\rho_A/\rho_B = -1.6$) shows that the changes in the properties of the proton donor and electron donor under the influence of substituents affect to an equal extent the strengths of the hydrogen bonds between thiophenols and acetophenones. The change in ΔH for the S–H...O=C hydrogen bond in this system is more sensitive to the change in the properties of the proton donor than in those of the electron donor.

In a study of the OH...O hydrogen bonds between *p*-substituted 2,6-di-t-butylphenols and anisoles or acetophenones[53], the opposite relation was obtained—the change in the OH...O bond strength was found to be more sensitive to changes in the properties of the electron donor. Comparison of the properties of the SH...O=C and OH...O=C hydrogen bonds reveals not only quantitative differences (the SH...O=C bond is weaker) but also qualitative differences—the changes in the properties of the proton acceptor and proton donor respectively play the main role in the variation of the OH...O=C and SH...O=C hydrogen bond strengths.

The hydrogen bond between thiophenol and acetic acid has been investigated[54] and the quantities $K^{45°} = 0.38$ (mole fraction)$^{-1}$, $-\Delta H = 1.2$ kcal mole^{-1}, and $-\Delta S = 5.9$ e.u. have been determined. Despite the much lower acidity of thiophenol than that of acetic acid ($pK_a = 6.52$ and 4.76 respectively[47]), thiophenol in fact functions as the proton donor and the acid as the electron donor. The reason for this is probably that OH...S hydrogen bonds, which the acid might form as the proton donor, cannot compete in strength with the OH...O=C bonds in the acid dimers, since electron-donating functions are appreciably weakened on passing from oxygen to sulphur[55-58].

The thermodynamics of the hydrogen bond being substituted thiophenols and thiobenzoic acids has been studied[59]. The latter differ sharply from acetic acid in the proton- and electron-donating properties. In this system too, it was also found that thiophenol behaves as the proton donor on formation of hydrogen bonds, while the thiolo-form of thiobenzoic acid is the electron donor despite the fact that thiophenol is the weaker acid. Of the two possible dimer structures



‡ The weak temperature variation of $\Delta\tau_C$ may be neglected[41,42].

structure (III) is apparently preferable, since hydrogen bonds of the type SH...S cannot compete with bonds of the type SH...O as regards strength. We may note that the effects of substituents (Table 3) are consistent with the proposed structure of the associated species.

Thus the available data[54,59] show that, when thiophenol is involved in association with acetic and thiobenzoic acids, and probably with other carboxylic acids, there is preferential formation of dimers in which thiophenol plays the role of the proton donor and the carbonyl group of the acid is the electron donor (SH...O=C). These bonds are probably stronger than the OH...S and even more so the SH...S hydrogen bonds, which might be formed if the acid and thiophenol changed roles, since the increase of electron-donating capacity when S is replaced by O has a greater effect on the energy of the hydrogen bond than the weakening of the proton-donating capacity on passing from OH to SH.[55]

Table 3. The spectroscopic and thermodynamic characteristics of the hydrogen bond in the association complexes of thiophenols with thiobenzoic acids.

R	$\Delta\tau_C$, p.p.m.	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
	R_A—C_6H_4SH+C_6H_5COSH		
2,5-$(CH_3)_2$	1.85	1.9	8.1
4-OCH_3	1.58	2.0	8.1
4-CH_3	2.08	2.1	9.6
H	1.52	2.1	8.3
4-Cl	1.70	2.2	9.3
2,5-Cl_2	1.75	2.5	11.4
	C_6H_5SH + R_B—C_6H_4COSH + CCl_4		
4-OCH_3	1.58	2.0	6.6
H	1.52	1.7	6.2
4-Cl	1.41	1.6	6.9

Thus the structure of the complexes and the properties of the hydrogen bonds are determined by the proton- and electron-donating capacities of the interacting components and not by their acidity or basicity, and in many cases the acidity and proton-donating capacity vary in opposition (for example, on passing from thiophenol to phenol the acidity decreases, while the proton-donating capacity increases sharply[60-62]).

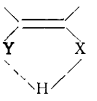
(c) The Intramolecular Hydrogen Bond

The presence of the intramolecular SH...B (B = O, N, or Cl) intramolecular hydrogen bonds in *o*-substituted thiophenols has been noted in a number of studies[63-69]. The NMR and infrared spectra as well as measurements of the dipole moments of a series of substituted thiophenols confirmed[70] the presence of an intramolecular hydrogen bond in *o*-halogeno-, *o*-methoxy-, *o*-nitro-, and *o*-methoxycarbonyl derivatives. The SH...B intramolecular hydrogen bond causes an appreciable increase in the intensity of the absorption band due to the vibrations of the SH group without a significant shift of the wavenumber. A much stronger hydrogen bond has been observed in *o*-methoxycarbonylthiophenol, in the molecule of which a six-membered chelate ring may be formed as a result of the intramolecular hydrogen bond.

It has been shown[71] that the SH group does not form an intramolecular hydrogen bond in α-mercaptocarboxylic acid esters, while a bond of this kind persists in thiosalicylic acid and its esters even in solution in acetonitrile. According to Ginzburg and Loginova[66], $-\Delta H$ = 0.9 kcal mole^{-1} for the S–H...O=C hydrogen bond in thiosalicylic acid.

In contrast to ω-*NN*-dialkylaminomercaptans[72], in aminothiophenols chelation is found to occur owing to the SH...N or NH...S hydrogen bonds[73]. It follows from the infrared spectra that such bonds are not formed in *o*-aminophenols or are significantly weaker. Consequently the proton- and electron-donating functions of sulphur are more effective than those of oxygen in the formation of intramolecular hydrogen bonds, while in association processes the opposite behaviour is observed. These findings are consistent with the calculations on intermolecular and intramolecular hydrogen bonds involving sulphur and oxygen atoms[74,75].

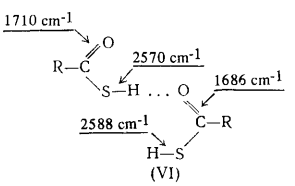
In rigid systems, such as five-membered chelates with intramolecular hydrogen bonds, the large size of the sulphur atom and diffuseness of its 3*p* orbitals ensure more satisfactory conditions than in oxygen for the overlapping of the interacting orbitals on formation of the bonds. Consequently the properties of the intramolecular hydrogen bonds



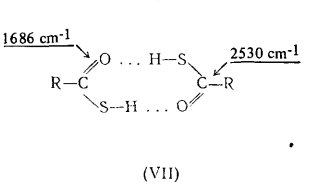
are determined by the nature of the proton donor and acceptor, the linearity of the XH...Y bond, and the distance between the donor and acceptor atoms[76].

2. THIOCARBOXYLIC AND PHOSPHOROTHIOIC ACIDS

Thiocarboxylic acids RC(O)SH should form more stable self-associated species than thiophenols and mercaptans via the SH...O=C hydrogen bonds. However, the literature data on this problem are contradictory. Thus it has been suggested[77] that the degree of self-association of thioacetic acid is low in view of the observed decrease of the wavenumber and increase of the intensity of the ν(SH) infrared band on passing from the gas to the liquid. In the gas phase[78] and in carbon tetrachloride solutions[79], no signs of the self-association of thioacetic acid were observed, which conflicts with the results of another study[80], where the intensities of the ν(C=O) and ν(SH) bands of thioacetic and thiobenzoic acid were found to vary with concentration, indicating unambiguously the formation of SH...O=C hydrogen bonds. The chemical shift of the SH protons was also found to depend on the concentration of thiobenzoic acid in benzene[81] and of thioacetic acid in carbon tetrachloride[82]. It has been suggested[83] that thioacetic and thiobenzoic acids form linear and cyclic dimers:



(VI)



(VII)

With decrease of temperature, the probability of the formation of the cyclic structure (VII) increases.

All the foregoing considerations suggest that the occurrence of the self-association of thiocarboxylic acids has been established. The present author[84,85] obtained by NMR data for the structures and thermodynamic characteristics of the hydrogen bonds in the self-associated species of *p*-substituted thiobenzoic acids. It was found that $-\Delta H = 6.2$ kcal mole^{-1} and $-\Delta S = 21$ e.u. for the unsubstituted acid. Comparison with data for benzoic acid[86] ($-\Delta H = 10.6$ kcal mole^{-1} and $-\Delta S = 18.8$ e.u.) showed that the S–H...O=C bonds are much weaker than the O–H...O=C bonds. On the other hand, thiobenzoic acids are much more self-associated than thiophenols and mercaptans. It has been shown[84] that the values of ΔH and ΔS for thiobenzoic acid represent the overall effect of the formation of two hydrogen bonds. Consequently the acid dimers have the cyclic structure (VII). These results apply solely to the thiolo-form of the acid (VIII), since in inert solvents the presence of the thiono-form (IX) was not observed[87,88].

In electron-donating solvents, the complex-formation process is accompanied by the formation of a new molecular structure with mobile protons, which are involved in rapid exchange with the protons of the OH groups of the solvent (methanol, acetic acid). This is probably associated with the formation of appreciable amounts of the thiono-tautomer owing to the displacement to the right of the equilibrium

$$\underset{\text{(VIII)}}{C_6H_5C(O)SH} \rightleftarrows \underset{\text{(IX)}}{C_6H_5C(S)OH}$$

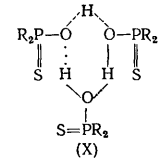
compared with the solution in carbon tetrachloride. The present author believes that this influence of electron-donating solvents on the state of the thiol–thione equilibrium should be sought by comparing the properties of the self-associated species and complexes formed with the solvent by the tautomeric species (VIII) and (IX).

As a result of complex formation with the electron donor (B), the self-associated species of the acid (VII) decompose. The associated species of the thiono-form $C_6H_5C(S)O–H..B$ produced under these conditions are more stable than those of the thiolo-form $C_6H_5C(O)S–H...B$, since the hydroxy-group is a more effective proton donor in the hydrogen bond than the mercapto-group. This in fact leads to the appearance in solution of an appreciable amount of the thione tautomer (IX).

The present author also investigated[85] the influence of substituents on the self-association of thiobenzoic acids (Table 4). The relation obtained between ΔH and the Hammett σ constants suggests that the change in the proton-donating capacity of the mercapto-group plays a decisive role in the alteration of the stability of the self-associated species of thiobenzoic acids. The change in the electron-donating capacity of carbonyl oxygen is of secondary importance and can affect only the magnitude but not the sign of the reaction constant ρ in the Hammett equation. For thiobenzoic acids, this quantity ($\rho = 1.8$) is significantly smaller than the value found[39] for the association of thiophenols with acetone ($\rho = 2.4$).

On passing from mono- to di-thiobenzoic acid, the tendency towards self-association decreases sharply. According to infrared spectroscopic data, all the signs of the self-association of dithiobenzoic acid vanish already in a 20% solution in carbon tetrachloride[89]. This can be explained by the fact that the SH...S=C hydrogen bond formed in dithiobenzoic acid dimers is much weaker than the S–H...O=C bond in monothiobenzoic acid dimers.

In contrast to thiocarboxylic acids, the monothio-derivatives of phosphorus-containing acids exist in inert solvents in the form of the thione tautomers[90]. The self-association of diethylphosphinothioic, *o*-ethyl methylphosphonothioate, and diethyl phosphorothioate has been investigated by NMR[91] in carbon tetrachloride solution on the basis of the temperature and concentration variation of the chemical shift of the hydroxyl protons. Analysis of these data by Lippert's method[92] showed that the main type of equilibrium in solutions of the above acids is monomer $\rightleftharpoons$ trimer. It was established that the values $-\Delta H \simeq 18$ established for the monothio-derivatives of phosphorus-containing acids correspond to the overall effect of the formation of three hydrogen bonds of the type OH...O and that the trimers have the cyclic structure



(X)

Consequently the thiophosphoryl sulphur cannot compete with the hydroxyl oxygen as the electron donor in the hydrogen bond.

Table 4. The spectroscopic and thermodynamic characteristics of the self-association of the acids *p*-$RC_6H_4C(O)SH$ in CCl_4 solution ($\Delta S = -21$ e.u.).

R	$\Delta\tau_c$, p.p.m.	$K^{27°}$, (mole fraction)$^{-1}$	$-\Delta H$, kcal mole^{-1}	σ
OCH_3	1.33	0.40	5.7	—0.268
H	1.33	0.95	6.2	0.000
F	1.34	0.95	6.2	0.062
Cl	1.32	1.83	6.6	0.227

Table 5. The spectroscopic and thermodynamic characteristics of the hydrogen bond in the self-associated species of organophosphorus monothio-acids $R_1R_2P(S)OH$.

R_1	R_2	τ_0, p.p.m.	$\Delta\tau_c$, p.p.m.	$10^{-3}K^{40°}$, (mole fraction)$^{-2}$	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
C_2H_5	C_2H_5	3.80	1.47	4.0	18.0	41.8
C_2H_5O	CH_3	4.39	2.00	5.7	17.8	40.5
C_2H_5O	C_2H_5O	4.47	2.19	10.0	18.0	39.4

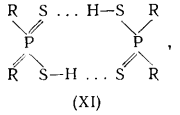
The data in Tables 4 and 5 show that, on passing from thiobenzoic acids to thio-derivatives of phosphorus-containing acids, there is a sharp increase of the ability to form self-associated species. This is due to the increase of the strength of the hydrogen bond when the mercapto-group is replaced by the hydroxyl as the proton donor, although this involves a significant gain in entropy, caused by the increased complexity of the structure of the self-associated species.

Thus the structures and properties of the self-associated species of monothio-acids depend on the position of the thiol–thione equilibrium. As stated above, in thiobenzoic acids the equilibrium is displaced towards the thiolo-tautomer, which results in the formation of the cyclic dimers (VII) with oxygen as the electron donor, similar to the carboxylic acid dimers[93]. For thio-derivatives of phosphorus-containing acids, the equilibrium is displaced towards the thiono-form, dimers of type (VII) becoming less stable owing to the reduced electron-donating capacity of sulphur and cyclic trimers (X), with oxygen as the donor, whose structure resembles that of the self-associated species of alcohols, are formed[94].

The self-association of dithio-derivatives of phosphorus-containing acids has been investigated in greater detail. Thus the infrared spectra of solutions of diethyl and dimethyl phosphorodithioates[95] and of phenyl phenylphosphonodithioate and ethyl ethylphosphonodithioate[89] in carbon tetrachloride showed a splitting of the ν(SH) band. The doublet structure of this band and the dependence of the relative intensities of its components on concentration and temperature were explained by the self-association of the acids with formation of SH...S bonds. Self-association of this type is assumed for both phosphorodithioic[96] and diphenylphosphinodithioic[97] acids. On the other hand, cryoscopic measurements have shown[98] that phosphorodithioic acids exist in benzene solutions as monomers. Presumably the decomposition of the self-associated species in this system is caused by the formation of complexes by the acid with the solvent (benzene). There is at present no doubt about the possibility of the formation of hydrogen bonds of the type SH...π.

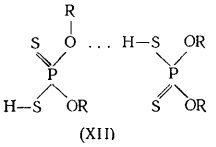
Many workers[99,100] believe that the doublet structure of the ν(SH) band is due to the presence of two rotational isomers with intramolecular hydrogen bonds between the SH groups and the oxygen atoms of the substituent or the sulphur atom in the P=S group.

Quantitative studies on the hydrogen bonds in the self-associated species of phosphorodithioic acids have been carried out by NMR and infrared spectroscopy. Thus a study has been made[101,102] of the hydrogen bond strengths in the self-associated species of a number of phosphorodithioic acids and in their complexes with dioxan. The authors[101,102] suggested the cyclic structure



(XI)

for phosphinodithioic acids and the linear dimeric structure

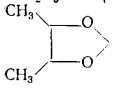


(XII)

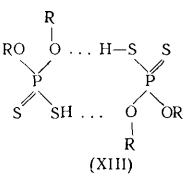
for the self-associated species of phosphonodithioic and phosphorodithioic acids. We may note, however, that the conclusion concerning the preferential formation of structure (XII), reached[101] on the basis of a comparison of the values of ν(SH) for self-associated species and complexes with dioxan as well as the hypothesis that the proton-accepting capacity of the oxygen in the RO substituent is greater than that of the thiono-sulphur in the P=S group appear to have little justification. One should also note that the same workers[102] believe that the thiophosphoryl group in phosphinic acids gives rise to more stable associated species than those produced by the oxygen of the substituent in phosphonic and phosphoric acids.

An NMR study has been made[103] of the self-association of dithio-derivatives of phosphorus-containing acids. In agreement with previous results[101,102], it was shown that the main type of equilibrium in solutions of these acids in carbon tetrachloride or cyclohexane is monomer $\rightleftharpoons$ dimer. The value of ΔH for self-association obtained by infrared spectroscopic (Table 6) and NMR methods (Table 7) agree satisfactorily when account is taken of the experimental error.

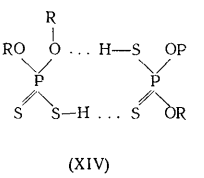
Table 6. The spectroscopic characteristics and strength of the hydrogen bonds formed by organophosphorus dithio-acids R_1R_2PSSH in their self-associated species and in their complexes with dioxan.

R_1	R_2	Self association		Complex with dioxan	
		$\nu_{SH...S(O)}$, cm^{-1}	$-\Delta H$, kcal mole^{-1}	$\nu_{SH...O}$, cm^{-1}	$-\Delta H$, kcal mole^{-1}
n-C_3H_7	n-C_3H_7	2405	3.2	2445	2.0
CH_3	C_6H_5	2405	3.4	2440	—
CH_3	CH_3O	2460	2.1	2470	—
CH_3	C_2H_5O	2460	2.1	2470	—
CH_3	n-C_3H_7O	2460	2.4	2470	—
CH_3	iso-C_3H_7O	2460	2.0	2470	—
C_2H_5	C_2H_5O	2460	2.3	2460	1.8
C_2H_5O	C_2H_5O	2460	2.1	2460	1.5
		2460	2.4	2450	1.8

The stability of the complexes (XI) of phosphinodithioic acids varies in the range 2.6–3.4 kcal mole^{-1}. Consequently the energy of the SH...S=P hydrogen bond is close to 1.5 kcal mole^{-1}. As already mentioned, in phosphonodithioic and phosphorodithioic acids, both thiono-sulphur and oxygen atoms in the substituent can behave as electron donors. For this reason, these acids can give rise to the following structures apart from complexes of types (XI) and (XII):



(XIII)



(XIV)

The conclusion[101,102] that the open-chain dimers (XII) are formed preferentially by phosphonic and phosphoric acids is inconsistent with thermodynamic data[101–103]. Thus the energy of the SH...O hydrogen bond between dithio-derivatives of phosphorus-containing acids and dioxan is 1.5–1.8 kcal mole^{-1}.[101] On the other hand, the strength of the bond of the same type but with the oxygen atom of the substituent at the phosphorus atom should be smaller, since in this case the electron-donating capacity of the oxygen atom is reduced owing to the effect of the $p\pi - d\pi$ conjugation[106,107]. Table 7 shows that the bond energy in the self-associated phosphonic and phosphoric acid species varies from 2.7 to 4.3 kcal mole^{-1}. Clearly

a structure of type (XII) with a single SH...O hydrogen bond cannot alone account for the observed heats of complex formation. On the other hand, cyclic structures of types (XI), (XIII), and (XIV) are consistent with experimental data. We therefore suggest that phosphonodithioic as well as phosphinodithioic acids form mainly cyclic dimeric self-associated species in solution in inert solvents. This conclusion is further confirmed by the similarity of the values of ΔS for self-association obtained for complexes of all three types of acids (Table 7).

Table 7. The spectroscopic and thermodynamic characteristics of the hydrogen bond in the self-association species of the acids R_1R_2PSSH.

R_1	τ_0, p.p.m.	$\Delta\tau_C$, p.p.m.	$K^{40°}$, (mole fraction)$^{-1}$	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.	pK_a^*	$-\Sigma\sigma_\Phi^{**}$
C_2H_5	8.07	2.75	1.4	2.7	8.0	5.06	2.202
C_6H_5	7.67	1.33	1.0	2.6	8.3	3.48	1.184
CH_3***	7.42	2.00	1.9	3.0	8.2	3.16	1.179
n-C_4H_9O	7.42	1.43	1.8	3.6	10.3	—	0.822
n-C_3H_7O	7.40	1.48	2.0	3.5	9.8	—	0.630
iso-C_4H_9O	7.34	1.27	1.4	3.5	10.5	—	0.600
iso-C_3H_7O	7.50	1.45	2.9	3.6	9.7	2.94	0.582
C_2H_5O	7.30	1.58	1.1	2.7	8.2	2.84	0.425
C_6H_5O	5.67	2.00	14.0	4.3	8.5	2.41	0.122

* Determined in 100% alcohol [104].
** Overall σ constants [105].
*** $R_2 = C_2H_5O$, in the remaining cases $R_1 = R_2$.

When data for the self-association of mono- and di-thio-derivatives of phosphorus-containing acids are compared, sharp differences are discovered [108]. The self-associated species of the monothio-derivatives have a trimeric cyclic structure formed by OH...O hydrogen bonds, while the dithio-acids give rise to cyclic dimers with SH...S and SH...O bonds. It was noted that, when oxygen is replaced by sulphur, both the electron-donating and the proton-donating capacity of the hydrogen bond are reduced. The sharp differences between the values of K, ΔH, and ΔS for the self-associated species investigated are therefore based not only on the differences in the numbers of the hydrogen bonds forming the complexes but also in their properties.

3. HYDROGEN BONDS AND RAPID PROTON EXCHANGE REACTIONS INVOLVING SH GROUPS

It was shown previously [55,109-111] that the initial stage of the proton transfer reaction between molecules or ions is the formation of an intermediate reaction complex in which the reactions centres of the interacting species are brought closer together by hydrogen bonds, which ensures the most favourable mutual orientation of the centres for the reaction. The increase of the strength of the hydrogen bond in the intermediate complex leads to a decrease of the height and width of the potential barrier to the reaction, which facilitates proton transfer via both the classical mechanism and as a result of the tunnel effect. These are also the causes underlying the observed correlations between the kinetic and activation parameters of rapid proton exchange reactions and the thermodynamic characteristics of the hydrogen bond between the exchanging reactants [55].

However, the dependence of the mechanism of the rapid proton exchange reactions on the structure of the complexes and the properties of the hydrogen bond between the exchanging components has still been inadequately investigated. This problem has been solved in a number of studies [54,59,120-122] for reactions involving SH, COOH, and COSH groups. Reactions of this type occupy an important place in various biochemical processes [123].

The kinetics and mechanism of the rapid proton exchange between the SH groups in a series of substituted thiophenols and the COOH group of acetic acid, catalysed by sodium acetate, have been investigated [54,120] by NMR. It was established that the rate-limiting stage of the reaction involves proton transfer from the thiophenol to the acetate ion in the bimolecular complex formed by hydrogen bonds:

$$PhSH \ldots {}^-OAc \rightleftarrows PhS^- \ldots HOAc. \qquad (3)$$

The increase of the rate constant and the decrease of the activation energy with enhancement of the electron-accepting capacity of the substituents in the thiophenol ring (Table 8) are consistent with the proposed exchange mechanism (3).

Table 8. The kinetic and activation parameters of the fast proton exchange reaction between ArSH and AcOH catalysed by sodium acetate.

Substituent	$10^{-2}\,k^{40°}$, litre mole^{-1} s^{-1}	E, kcal mole^{-1}	lg A
2,5-$(CH_3)_2$	4.3	10.1	9.7
4-OCH_3	10.5	9.5	9.7
H	16.2	9.3	9.7
4-Cl	49.0	8.9	9.9
2,5-Cl_2	169.8	8.8	10.4

It is of interest to compare these data with the results of studies on the proton exchange between thiophenols and methanol in an alkaline medium [124] which proceeds in the trimolecular complex

$$ArSH \ldots \underset{|}{\overset{CH_3}{O}}H \ldots {}^-SAr \qquad (XV)$$

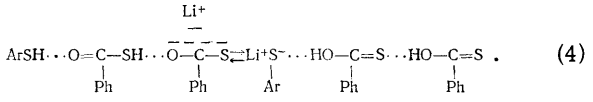
and its rate is limited by proton transfer from the thiophenol to the alcohol. The activation energy is in this case much more sensitive to the influence of the substituents in the thiophenol ring than in reaction (3). This can be explained by the levelling of the strengths of the AH...B hydrogen bonds involving a strong electron donor (for example $B = OH^-$ or AcO^-) and differing in the strengths of the proton donors, like the differences between the acid strengths in highly basic solvents. The activation energies for the exchange reaction involving such hydrogen bonds, which depend on the strength of the latter, are therefore also levelled.

The proton exchange between the SH and COOH groups in thiolactic acid $CH_3CH(SH)COOH$, between 1-methylethanethiol and acetic acid [121], and in mercaptoacetic acid $HSCH_2COOH$ [122] takes place in a binary complex of type (3)

when the process is catalysed by sodium acetate. The values of k, E, and $\lg A$ are listed below:

Compound	$10^{-2}k$, litre mole^{-1} s^{-1}	E, kcal mole^{-1}	$\lg A$
Thiolactic acid	3.6 (42° C)	11.8	10.7
1-Methylethanethiol	0.1 (46° C)	14.2	10.8
Mercaptoacetic acid	7.1	12.4	8.5

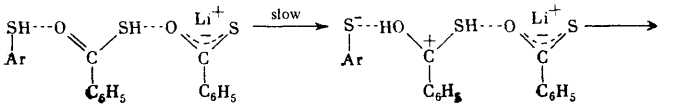
The proton exchange between a series of thiophenols and thiobenzoic acid, differing sharply from acetic acid in its proton- and electron-donating properties, has been investigated[59] and it has been established that, when the process is catalysed by lithium thiobenzoate, its rate-limiting stage involves proton transfer in the trimolecular complex formed by hydrogen bonds:



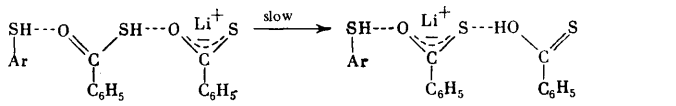
(4)

This complex arises as a result of the association of the dimers $C_6H_5SH\cdots O{=}C(SH)C_6H_5$ (III) present in the system with lithium thiobenzoate, since trimolecular collisions of thiophenol, acid, and catalyst molecules are unlikely. The formation of the complex or its decomposition cannot limit the rate of exchange, since they are rapid reactions involving the formation or dissociation of hydrogen bonds.

The data obtained for the influence of substituents on the kinetics of reaction (4) provided evidence in support of a detailed exchange mechanism. Three schemes are possible: single-stage synchronous transfer of two protons [reaction (4)] and two-stage ionisation schemes [reactions (5) and (6)], in the slow stage of which the thiobenzoic acid or catalyst molecule is protonated:



(5)



(6)

Scheme (6) is inconsistent with the influence of substituents on the rate of reaction, since the rate of the slow stage in this scheme should not depend on the substituents in the thiophenol ring. On the other hand, mechanisms (4) and (5) are consistent with experimental data. Furthermore, a quantitative relation has been observed between the kinetic parameters of the exchange reaction and the thermodynamic characteristics of the hydrogen bond in the dimeric species formed by thiophenols with thiobenzoic acid (Tables 3 and 9). This relation presupposes proton transfer in the slow stage via the S–H...O=C hydrogen bond [see scheme (5)].

We may note that a considerable similarity between the kinetics and mechanisms of the rapid proton exchange reactions of thiophenols with thiobenzoic acid[59] and methanol[124,125] has been observed. In both cases, the rate of reaction is described by a third-order kinetic equation, the substituents in the thiophenol ring have the same type of influence, and even the corresponding catalytic rate constants and activation energies are similar. Presumably, such analogy is due to the similarity of the slow stages in the above processes—proton transfer via the SH...O hydrogen bond in accordance with a type (5) mechanism.

Table 9. The kinetic and activation parameters of the fast proton exchange reaction between substituted thiophenols and thiobenzoic acid catalysed by lithium thiobenzoate.

Substituent	$10^{-3}\,k^{40°}$ litre mole^{-1} s^{-1}	E, kcal mole^{-1}	$\lg A$
2,5-$(CH_3)_2$	4.6	8.7	9.8
4-OCH_3	13.6	8.0	9.7
4-CH_3	13.1	7.8	9.6
H	20.9	7.8	9.8
2,5-Cl_2	140.0	4.8	8.5

In contrast to the above similarity, the exchange of thiophenols with thiobenzoic acid differs as regards kinetics and mechanism from the seemingly analogous proton exchange reaction between thiophenols and acetic acid. The weak hydrogen bond between thiophenol and acetic acid and the marked tendency of the latter to undergo self-association cause the alkali-catalysed rapid proton exchange involving the SH and COOH groups to proceed via the bimolecular mechanism (3), the acetic acid molecule not being involved in the slow stage. On the other hand, the stronger hydrogen bond between thiophenol and thiobenzoic acid and the much smaller (compared with acetic acid) tendency of the latter towards self-association explains why the proton exchange between the SH and COSH groups take place in a trimolecular hydrogen-bonded complex.

Thus the data examined in this section constitute undoubted proof that the properties of the hydrogen bond between the exchanging components determine not only the kinetics but also the characteristics of the mechanism of rapid proton exchange.

4. THE ELECTRON-DONATING CAPACITY OF SULPHUR COMPOUNDS

The proton- and electron-donating properties of the hydrogen bond formed by the SH groups of mercaptans, thiophenols, and thiocarboxylic acids, as well as the thio-derivatives of phosphorus-containing acids were examined above. Other types of sulphur compounds, for example sulphides R_2S, thioketones $R_2C{=}S$, phosphine sulphides $R_3P{=}S$, etc. do not have a mobile proton but can nevertheless form hydrogen bonds as electron donors by virtue of the lone electron pairs of the bivalent sulphur atom.

Convincing evidence for the association of sulphur compounds of this type with various proton donors has been compiled in the literature[12]. For example, the OH...S,[126-128] OH...S=P,[129] OH...S=C,[130,131] NH...S,[132] and CH...S[133]

bonds have been discovered. The electron-donating properties of the hydrogen bonds formed by amines, ethers, and sulphides (thioethers) with phenols and alcohols have been compared[134-140].

The values of ΔH quoted in Table 10 show that the electron-donating capacity of the hydrogen bonds formed by amines is twice as great and that of the bonds formed by ethers approximately 1.5 times as great as that of the bonds involving sulphides.

Table 10. Hydrogen bond strengths in the complexes of amines, ethers, and sulphides with alcohols and phenols.

Electron donor	$-\Delta H$, kcal mole^{-1}	Electron donor	$-\Delta H$, kcal mole^{-1}
$(CF_3)_3COH$ [calorimetry (Ref.134)]		p-ClC_6H_4OH [i.r. (Refs.137-139)]	
$(C_2H_5)_3N$	14.3	$(C_2H_5)_3N$	9.5
$(C_2H_5)_2O$	8.3	$(C_4H_9)_2O$	6.3
$(C_2H_5)_2S$	7.0	$(C_2H_5)_2S$	5.0
p-$CH_3C_6H_4OH$ [i.r. (Ref. 137, 138)]		$(CF_3)_2CHOH$ [i.r., calorimetry (Ref.137, 140)]	
C_5H_5N	7.8	$(C_2H_5)_3N$	11.5
$(C_4H_9)_2O$	5.9	$(C_2H_5)_2O$	7.2
$(C_2H_5)_2S$	4.3	$(CH_2)_4S$	5.8
$(CH_2)_4S$	4.6	C_3H_7OH [GLC (Ref.136)]	
C_6H_5OH [i.r. (Ref.137, 138)]		$(C_8H_{17})_2CH_3N$	5.1
$(C_2H_5)_3N$	9.1	$(C_8H_{17})_2O$	3.8
$(C_2H_5)_2O$	6.0	$(C_8H_{17})_2S$	2.4
$(C_4H_9)_2O$	6.0	C_4H_9OH [GLC (Ref.136)]	
$(C_2H_5)_2S$	4.6	$(C_8H_{17})_2CH_3N$	5.3
p-FC_6H_4OH [i.r. (Ref.137, 139)]		$(C_8H_{17})_2O$	3.8
$(C_2H_5)_3N$	9.0	$(C_8H_{17})_2S$	2.8
$(C_2H_5)_2O$	5.6	$(CH_3)_3COH$ [GLC (Ref.136)]	
$(C_2H_5)_2S$	4.7	$(C_8H_{17})_2CH_3N$	4.0
m-FC_6H_4OH [i.r. (Ref.138)]		$(C_8H_{17})_2O$	3.1
$(C_4H_9)_2O$	6.0	$(C_8H_{17})_2S$	2.0
$(C_2H_5)_2S$	5.0		

The data obtained have been analysed[136] with the aid of the Drago relation[141]

$$-\Delta H = E_A\ E_B + C_A\ C_B, \qquad (7)$$

where the empirical parameters E_A and C_A refer to the proton donor and E_B and C_B refer to the electron donor. The values of E_A and E_B characterise the ability of the donor and acceptor to enter into an electrostatic interaction, while C_A and C_B determine the contribution to the overall bond energy by the donor–acceptor (covalent) forces. Calculation of the contributions of the electrostatic ($-\Delta H_E = E_A E_B$) and donor–acceptor ($-\Delta H_C = C_A C_B$) interactions to the overall energy of the hydrogen bond showed that, when dioctyl ether, methyldioctylamine and dioctyl sulphide are involved in association with aliphatic alcohols, the contributions of the electrostatic forces to the overall energy of the hydrogen bond are 83, 56, and 34% respectively. Consequently, according to Pearson's classification[142], ethers are "hard" bases, sulphides are "soft" bases, while amines are "hard-soft" bases.

The electron-donating capacities of ethers and sulphides in relation to alkyl halides have been compared[143]. The data obtained by gas–liquid chromatography (GLC) are difficult to interpret in terms of the hypothesis that complexes are formed in this system only via the C–H...O and C–H...S hydrogen bonds. Thus the stabilities of the complexes formed by chloroform with di-n-octyl ether and di-n-octyl sulphide are 2.38 and 1.93 kcal mole^{-1} respectively. These values agree with the usual hypothesis that the electron-donating capacity in the hydrogen bond decreases on passing from oxygen to sulphur[12,55]. On the other hand, the complex of bromoform with the ether ($-\Delta H$ = 2.17 kcal mole^{-1}) proved to be less stable than that with the sulphide ($-\Delta H$ = 2.28 kcal mole^{-1}). Furthermore, the replacement of chloroform by bromoform leads to a decrease of the stability of the ether complex in accordance with the reduced proton-donating capacity of bromoform relative to chloroform[144-147], while the opposite behaviour applies to the sulphide—the bromoform complex is more stable than the chloroform complex. In order to account for the above findings, the authors[143] assume that in the association of halogenoalkanes with ethers and particularly with sulphides complexes with charge transfer of the $n \rightarrow \sigma^*$ type[148] between the oxygen or sulphur atoms (n-electron donor) and halogen atoms (electron acceptor) are formed in addition to the hydrogen bond. The contribution of the charge-transfer interaction increases and the tendency towards the formation of hydrogen bonds diminishes on passing from the ether to the sulphide and from chloroform to bromoform. Possibly the classic electrostatic interaction, which may be enhanced with increase of atomic polarisability on passing from O to S and from Cl to Br, plays an important stabilising role for such relatively weak "contact" complexes[149,150].

The hydrogen bonds between phenylacetylene and ethers and sulphides have been investigated[133] by NMR and infrared spectroscopy. The formation constants of the 1 : 1 complexes formed by sulphides are approximately five times smaller than those of the complexes formed by ethers.

Table 11. The thermodynamic characteristics of the hydrogen bonds formed by chloroform, phenol, and ethanol with certain sulphides and disulphides.

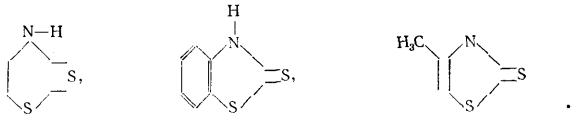
Electron donor	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.	Electron donor	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
Cl_3CH [NMR (Ref.151)]			C_6H_5OH [i.r. (Ref.153)]		
$(CH_3S)_2$	0.93	7.0	$(CH_3S)_2$	2.30	6.2
$(C_2H_5)_2S$	1.70	9.0	$(C_4H_9)_2S$	4.90	16.6
$(CH_2)_4S$	2.30	10.9	C_2H_5OH [i.r. (Ref.153)]		
Cl_3CH [NMR (Ref.152)]			$(CH_3S)_2$	1.50	—
$(CH_3)_2S$	1.50	—	$(C_4H_9)_2S$	2.60	—
$(C_2H_5)_2S$	2.10	—			

The electron-donating capacities in the hydrogen bonds of sulphides and disulphides may be compared on the basis of the available data[151-153] (Table 11). It is striking that the strength of the hydrogen bond diminishes approximately by a factor of two on passing from sulphides to disulphides. The chemical bond between two sulphur atoms weakens their electron-donating properties. This observation was made for the first time by Epshtein and Zhdanova[153], but has not been explained. The present author believes that the cause of the weakening of the electron-donating capacity of disulphides may be as follows. The multiplicity of the chemical bonds between two sulphur atoms may increase, because, apart from a single σ bond, there is a possibility of interaction of the π-type between the 3p orbital of the lone electron pair of one atom and the vacant 3d orbital of another, which is suitable as

regards symmetry. Such interaction must lead to an increase of the degree of delocalisation of the 3*p* electrons and hence to a decrease of the orbital electron density. This entails a decrease of the capacity of the 3*p* orbital of the lone electron pair of the sulphur atom for overlapping with the 1*s* orbital of the hydrogen atom of the proton donor, which leads in its turn to the weakening of the hydrogen bond noted above. An increase of the amount of double bond character in S–S in disulphides is indicated by the data quoted in Foss's paper[154].

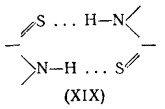
Hydrogen bonds involving the electron-donating C=S, P=S, and As=S groups have been investigated[155-161]. The abilities of certain enaminothiones to form hydrogen bonds has been compared in an infrared spectroscopic and NMR study[155] with those of the corresponding oxo-analogues. It was observed that the efficiency of the thiono-group as an electron donor may be less effectively reflected in an intermolecular hydrogen bond than in the case of the carbonyl group. The opposite is true of intramolecular conjugated chelate systems, which has been attributed to the 6π-electron stabilisation of the chelate, including the expansion of the orbital of the sulphur atom.

Hydrogen bonds of type N–H...S=C have been discovered[157] in the self-associated species of the heterocyclic thioamides (XVI)–(XVII):



(XVI) (XVII) (XVIII)

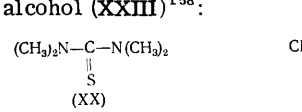
According to X-ray diffraction data[162], 2-mercaptobenzothiazole (XVII) forms centrosymmetric cyclic dimers with a short hydrogen bond. The infrared spectra of the thioamides (XVI)–(XVIII) hardly change on passing from crystals to a dilute solution in carbon tetrachloride. The cyclic dimeric structure of the associated species



(XIX)

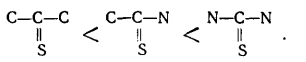
probably persists also in carbon tetrachloride solution. The intensity of the ν(NH...S) bands and the values of $\Delta\nu = \nu(HN) - \nu(NH...S)$ show that the strength of the hydrogen bond in complexes of type (XIX) increases in the sequence (XVI) < (XVII) < (XVIII). This conclusion is consistent with the observed dimerisation constants, which are 88, 570, and 5540 litre mole^{-1} for complexes (XVI), (XVII), and (XVIII) respectively, and the results of a study[163] of the influence of hydrogen bonds on the ultraviolet spectra of the same compounds.

The OH...S=C hydrogen bond has been investigated calorimetrically in relation to the association of tetramethylthiourea (XX) and *NN*-dimethylthioacetamide (XXI) with alcohols—hexafluoroisopropyl alcohol (XXII) and trifluoroethyl alcohol (XXIII)[158]:

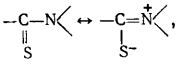


(XX) (XXI)

The energies of the OH...S=C hydrogen bond in the associated species formed by compound (XX) with compounds (XXII) and (XXIII) are 6.5 kcal mole^{-1} ($\Delta\nu$ = 445 cm^{-1}) and 4.6 kcal mole^{-1} ($\Delta\nu$ = 290 cm^{-1}), while the energies of the bond of the same type in the complexes formed by compound (XXI) with compounds (XXII) and (XXIII) are 6.0 kcal mole^{-1} ($\Delta\nu = 430$ cm^{-1}) and 4.3 kcal mole^{-1} ($\Delta\nu = 280$ cm^{-1}). According to the literature[164], the bond energies in the complexes formed by phenol with alkylthioureas are 4–4.8 kcal mole^{-1}. Comparison of Sherry and Purcell's data[158] with those of Singh et al.[44] showed that the electron-donating capacity of sulphur increases in the sequence



This is probably associated with the increasing contribution of the electrostatic interaction to the energy of the OH...S=C hydrogen bond in the above series owing to the greater contribution of the dipolar structure in thioamides



than in thioketones.

The electron-donating capacity of sulphur in the P=S and As=S groups has been investigated by infrared spectroscopy and calorimetry in a number of studies[158-160] (Table 12). The enthalpies of formation of the hydrogen bond with phenol have shown that the electron-donating capacity of the As=S group is only slightly greater than that of the P=S group and much smaller than that of the As=O group with similar substituents.

Table 12. The hydrogen bond strengths and the ν(OH) band shifts in the complexes formed by phenol and fluorinated alcohols with thio-derivatives of phosphorus-containing acids, phosphine sulphides, and arsine sulphides and oxides.

Electron donor	Δν, cm^{-1}	−ΔH, kcal mole^{-1}	Electron donor	Δν, cm^{-1}	−ΔH, kcal mole^{-1}
C_6H_5OH[159]			CF_3CH_2OH[158]		
$(C_2H_5)_3P=S$	321	5.9	$(C_4H_9)_3P=S$	273	4.4
$(C_2H_5O)_2C_6H_5P=S$	261	5.1	$(C_8H_{17})_3P=S$	272	4.3
$(C_2H_5O)_3P=S$	196	4.6	$(C_6H_5)_3P=S$	200	—
$(C_2H_5S)_3P=S$	191	4.6	C_6H_5OH[160]		
$(C_6H_5Cl_2P=S$	186	4.3	$(C_2H_5)_3As=S$	369	6.2
$(CF_3)_2CHOH$[158]			$C_6H_5(C_2H_5)_2As=S$	343	5.9
$(C_4H_9)_3P=S$	423	6.3	$(C_6H_5)_2C_2H_5As=S$	321	5.7
$(C_8H_{17})_3P=S$	414	5.9	$(C_6H_5)_3As=S$	296	5.5
$C_6H_5)_3P=S$	312	4.6	$(C_6H_5)_3P=S$	241	4.9
			$C_6H_5(C_2H_5)_2As=O$	711	8.6

The empirical parameters E_B and C_B [see Eqn. (7)] for the sulphur-containing bases investigated have been calculated[158]. As was to be expected, the parameters found for S donors differ significantly from the corresponding characteristics of "hard" oxygen- and nitrogen-containing donors, namely in the case of sulphur the parameters C_B are greater and the E_B are smaller. This implies that the covalent contribution to the strength of the hydrogen bond involving an S donor plays a decisive role. This conclusion is consistent with results[136] according to which S donors are classified as "soft" bases.

III. VARIATION OF THE PROTON- AND ELECTRON-DONATING CAPACITIES IN SERIES OF COMPOUNDS OF THE SAME TYPE FORMED BY GROUP V–VII ELEMENTS

1. GROUP V ELEMENTS

The electron-donating properties in the hydrogen bonds formed by compounds of Group V elements, with the exception of nitrogen, have been very little investigated. Nevertheless, the available literature data[165,166] make it possible to trace certain regularities in the variation of the electron-donating capacities of analogous nitrogen, phosphorus, arsenic and antimony compounds. In the studies quoted, the association of pyrrole, phenol, and methanol with the electron donors $(C_2H_5)_3Y$ (Y = N, P, As, or Sb) was investigated and it was found that all the compounds form hydrogen bonds with the proton donors. Antimony and even arsenic exhibit semimetallic properties, but form hydrogen bonds nevertheless. There is probably a significant contribution of the *p* or *d* orbitals to that of the free electron pair of antimony, imparting to the latter directional properties, which are required in the formation of the hydrogen bond.

According to the data in Table 13, the electron-donating capacity in the N–H...Y (Y = N, P, As, or Sb) hydrogen bond decreases in the sequence $(C_2H_5)_3N > (C_2H_5)_3P > (C_2H_5)_3As > (C_2H_5)_3Sb$. This might have been expected, since the fundamental properties change in the same direction[167] and the formation of the hydrogen bond is the first stage in the acid-base interaction with proton transfer[168].

Table 13. Characteristics of the hydrogen bonds formed by pyrrole and phenol with R_3Y.

Y	$\Delta\nu$, cm^{-1}	$K^{30°}$, litre mole^{-1}	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
		Pyrrole, N–H...Y		
N	310	—	—	—
P*	216	1.53	—	—
P	166	0.89	3.0	10.0
As	101	0.37	2.5	10.0
Sb	65	0.23	—	—
		Phenol, O–H...Y		
N	556	90.00	9.1	—
P	333	4.50	4.3	11.0
As	219	1.01	3.4	11.0
Sb	155	0.43	2.9	11.0

*R = n-C_4H_9, in the remaining cases R = C_2H_5.

The significant discrepancy between the very large change in basicity and the relatively small change in electron-donating capacity in the R_3Y series has been discussed[165]. For example, the difference between the basicities of $(C_2H_5)_3P$ and $(C_2H_5)_3As$ amounts to 5 pK units, while the association constant changes only by a factor of 2.5. There exist two alternative explanations of the variation of the basicity in the series of analogous compounds of the elements belonging to the same Group: either in terms of the Gibbs rehybridisation theory[169] or in terms of the theory of electron correlation repulsion[167]. Both theories are based on allowance for the electronic configuration of the central atom (the reaction centre of the base) in the proton transfer. According to Gurka and Taft's results[170], the formation of the hydrogen bond can be regarded as only partial proton transfer, since the electronic configuration of the central atom changes in this process to a much lesser extent than on protonation. Hence follows the small change in electron-donating capacity on formation of the hydrogen bond.

As will be seen below, there are other explanations in the literature of the insignificant change in electron-donating capacity on transition from, say, phosphorus to arsenic or from sulphur to selenium, based, in particular, on the examination of the contributions of various mechanisms to the redistribution of electron density between the proton donor and electron donor on complex formation.

The nature of the changes in electron-donating capacity in the O–H...Y[166] and N–H...Y[165] (Y = N, P, As, or Sb) bonds is the same. The values of $\Delta\nu$, K, and ΔH (Table 13) show that the electron-donating capacity of Y in the O–H...Y bond diminishes in the sequence N > P > As > Sb. The greatest changes in the above quantities occur in the transition from nitrogen to phosphorus. Arsenic and antimony are characterised by similar electron-donating capacities. This may be associated with the increase of the polarisability of the orbital of the free electron pair on passing to heavier elements in Group V, which leads to an increase of the contribution of dispersion forces to the energy of the hydrogen bond. At the same time the charge-transfer interaction may be intensified, since the ionisation potential of Y diminishes.

It is noteworthy that the Badger–Bauer rule[171] holds for the A–H...Y hydrogen bonds (Y is a Group V element), since there is a linear correlation between $\Delta\nu$ and ΔH.

The proton-donating capacities of compounds with X–H (X = N, P, or As) groups have been investigated only for X = N. There have been no direct experimental studies on the properties of the X–H...B hydrogen bond with X = P or As. There are only indirect data which suggest that, on passing from amines to phosphines or from ammonium to phosphonium compounds, the proton-donating capacity of X–H falls. Such studies include those of the rapid proton exchange between trimethylphosphonium ions and water[172] or between dimethylphenylphosphonium ions and methanol[173]. The results of these studies have been examined in detail in a review[55] and compared with those for the analogous reactions involving N–H bonds.

A sharp decrease of proton-donating capacity on passing from N–H to P–H is indicated by the *ab initio* calculations[27] of the energy of the hydrogen bond in the ammonia and phosphine complexes with the hydrides of the electronegative elements in the Second and Third Periods. For example, $-\Delta H$ = 4.07 kcal mole^{-1} for the complex H_2N–H...OH_2, while for the complex H_2P–H...OH_2, $-\Delta H$ is only 1.06 kcal mole^{-1}.

The problem of the type of change in proton-donating capacity on passing from P–H to As–H still remains unresolved.

2. GROUP VI ELEMENTS

The first quantitative studies on the relative electron-donating capacities in the hydrogen bonds formed by analogous compounds of Group VI elements include those of West and coworkers[174,175], where the thermodynamic characteristics of the hydrogen bonds between phenol and the electron donors $(n\text{-}C_4H_9)_2Y$ or $(t\text{-}C_4H_9)_2Y$ (Y = O, S, Se or Te) were determined by infrared spectroscopy. It

was shown for the first time that the atoms of heavy Group VI elements behave as electron donors in the formation of the OH...Se and OH...Te hydrogen bonds.

The replacement of oxygen by sulphur or selenium lowers significantly the strength of the hydrogen bond with phenol (Table 14). The maximum difference between the values of ΔH is observed on passing from oxygen to sulphur.

Table 14. Characteristics of the hydrogen bonds between phenol and dibutyl chalcogenides R_2Y[175] (the results of West et al.[174] are given in brackets).

Y	$\Delta\nu$, cm^{-1}	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
O	278	5.71 (5.98)	15.5 (11.8)
S	254	4.19 (4.26)	13.5 (9.0)
Se	240	3.69 (3.72)	14.9 (7.6)
Te	220	—	—
O*	—	7.31	22.0
S*	—	4.87	12.2

*R = t-C_4H_9, in the remaining cases R = n-C_4H_9.

It is striking that the values of ΔH found by West and coworkers[174,175] are virtually the same, while the values of ΔS diverge significantly. According to Pimentel and McClellan[1], values of $-\Delta S$ in the range 8–12 e.u. are the most probable for hydrogen bonds having average energies between 4 and 6 kcal mole^{-1}. The values of ΔS quoted in the second study by West et al.[175] are apparently too low (i.e. their absolute values are too high), while the earlier results[174] are more correct. The measured values of $\Delta\nu$ agree with the results of later investigations[176].

Table 15. The spectroscopic and thermodynamic characteristics of the hydrogen bonds formed by phenol and indole with diethyl chalcogenides $(C_2H_5)_2Y$.

Y	$\Delta\nu$, cm^{-1}	$\Delta k/k$	$K^{40°}$, litre mole^{-1}	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
		Phenol, O-H...Y			
O	274	0.146	4.50	5.63	14.9
S	251	0.134	0.80	3.35	11.1
Se	236	0.126	0.62	3.15	11.1
Te	213	0.114	0.50	—	—
		Indole, N-H...Y			
O	155	0.860	1.72	—	—
S	136	0.760	0.72	—	—
Se	132	0.740	0.69	—	—
Te	130	0.730	0.48	—	—

Note. $\Delta k/k \simeq 2\Delta\nu/\nu_0$ is the relative change in the force constant of the O–H or N–H bond on formation of the hydrogen bond[178].

The hydrogen bonds formed by phenol and indole with diethyl ether and its sulphur, selenium and tellurium analogues have been investigated by NMR and infrared spectroscopy[177]. It was found that the N–H group in indole and the O–H group in phenol form hydrogen bonds not only with oxygen and sulphur but also with selenium and tellurium. Chojnowski and Brandt[177] attempted to analyse the results (Table 15) in order to determine which type of interaction—electrostatic or charge-transfer—makes the main contribution to the energy of the hydrogen bond. It was suggested that the contribution of the electrostatic interaction to the A–H...$Y(C_2H_5)_2$ hydrogen bonds (A–H is a constant moiety and Y = O, S, Se or Te) should decrease on passing from oxygen to tellurium, since the negative charge on the electron-donating atom diminishes in the same sequence, but the contribution of charge transfer to the overall bond energy should then increase, since the ionisation potential of Y diminishes.

Table 15 shows that all the characteristics of the complex-formation reactions ($\Delta\nu$, $\Delta k/k$, K, and ΔH) decreases from oxygen to tellurium. Consequently the electron-donating capacity of Y in the hydrogen bond diminishes in the sequence O > S > Se > Te.

Since $\Delta k/k \simeq b^2$, where b is the coefficient defining the contribution of the state with electron transfer to the overall wave function of the complex[179,180], i.e.

$$\psi = a\varphi(AB) + b\varphi(A^-B^+), \qquad (8)$$

the observed decrease of $\Delta k/k$ and hence of the coefficient b [Eqn. (8)] from oxygen to tellurium implies a decrease of the contribution to the overall energy of the hydrogen bond due to the charge-transfer interaction. It is believed[177] that the interaction of this type is not of decisive importance in the formation of hydrogen bonds, since the increase of the H...Y bond length from oxygen to tellurium causes a greater decrease of its strength than the postulated increased influence of charge transfer on ΔH as the ionisation potential of Y diminishes[181].

According to Pogorelyi et al.,[182] butyl chalcogenides form hydrogen bonds not only with the proton-donating OH and NH groups but also with the mercapto-group of thiophenol. As was to be expected, the strength of the SH...Se and SH...Te bonds is lower than that of the OH...Se and OH...Te bonds. The values of ΔH for the complexes investigated (Table 16) diminish in the sequence O > S > Se > Te.

Table 16. The thermodynamic parameters of the hydrogen bonds formed by 2,6-di-t-butylphenyl (ArOH) and thiophenol with di-n-butyl chalcogenides $(n\text{-}C_4H_9)_2Y$.

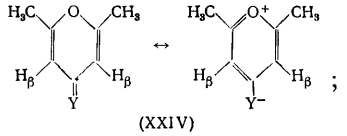
Y	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
	C_6H_5SH		ArOH	
O	2.7	10.3	3.8	13.2
S	2.4	8.1	3.3	11.7
Se	2.3	8.1	3.3	12.0
Te	2.1	7.9	3.1	12.2

The observed[175-177,182] decrease of the electron-donating capacity of Group VI elements with increase of n (the principal quantum number of the orbital of the free electron pair of Y) is probably an indication that the main contribution to the energy of the A–H...Y hydrogen bond (Y = O, S, Se, or Te) comes from the redistribution of the charge owing to the overlapping of the 1s orbital of the bridging hydrogen atom with the $np\sigma$ orbital of Y.[181] With

increase of n, the p electrons become more diffuse, and their orbital density decreases, with a consequent decrease of the capacity of the corresponding orbitals for overlapping and there is an appreciable intensification of the repulsion forces between A and Y due to the inner electrons of Y.

However, the above treatment does not rule out another explanation—the decrease of ΔH in the sequence O > S > Se > Te may be caused by the weakening of the electrostatic interaction, since the negative charge diminishes from oxygen to tellurium.

In this connection, the results of a study of hydrogen bonds involving 2,6-dimethyl-4-pyrone and its thio- and seleno-analogues are of interest[183-185]:



(XXIV)

Y=O, S, or Se .

Compounds of the type of the pyrone (XXIV) differ from dialkyl chalcogenides by the presence of an appreciable negative charge, localised on the electron-donating centre—the exocyclic oxygen, sulphur, or selenium atom[184], which may affect the relative contributions of different types of interactions to the hydrogen bond energy.

Table 17 shows that the results obtained by the NMR[185] and infrared spectroscopic[184] methods agree satisfactorily. For both phenol and methanol, the strength of the hydrogen bond decreases in the sequence pyrone > thiopyrone > selenopyrone. In conformity with its greater proton-donating capacity, phenol forms more stable complexes than methanol.

Table 17. The spectroscopic and thermodynamic characteristics of the hydrogen bonds in the association complexes of 2,6-dimethyl-4-pyrone and its thio- and seleno-analogues with methanol and phenol.

Proton donor	τ_0, p.p.m.	τ_C, p.p.m.	$K^{40°}$, litre mole^{-1}	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
		Pyrone, OH...O			
CH_3OH	4.15	3.87	4.3	4.8	12.1
C_6H_5OH	4.15	3.76	7.4	5.5*	10.5*
		Thiopyrone, OH...S			
CH_3OH	3.26	3.07	0.9	3.6	11.6
C_6H_5OH	—	—	—	4.8*	4.5*
		Selenopyrone, OH...Se			
CH_3OH	2.89	2.67	1.0	3.1	9.7
C_6H_5OH	—	—	—	3.9*	4.8*

Note. τ_0 and τ_C are the chemical shifts of the -Hβ protons of the pyrone derivatives investigated in the monomer and complex respectively.
*Infrared spectroscopy; NMR was used in the remaining cases.

The dependence on n of ΔH for the hydrogen bonds between different proton donors and bases where the electron-donating centres are Group VI elements is similar for the pyrones (XXIV) and dialkyl chalcogenides. The strength of the hydrogen bond and hence the electron-donating capacity decrease with increase of n. The present author believes that these data demonstrate that the mechanism of the redistribution of electron density owing to charge transfer from the highest occupied orbital of the electron donor to the antibonding σ orbital of the A–H bond does not play a decisive role in the formation of the hydrogen bond between the atoms of Group VI elements, regardless of the structure of the electron donor molecule.

Thus the electron-donating properties of Group VI elements are determined mainly by the overlapping between the 1s (H) and np (Y) orbitals. This conclusion is confirmed by the correlation between the strength of the hydrogen bonds formed by ethers and sulphides with the integral for the overlap of the orbital of the np electrons of the oxygen and sulphur atoms with the 1s orbital of the bridging hydrogen atom[186].

Together with the redistribution of the charge via the orbital overlapping mechanism, there is also a change in the contribution to ΔH by the electrostatic interaction. The negative charge on the heteroatom decreases approximately by a factor of two on passing from oxygen to tellurium in dialkyl chalcogenides[177]. On the other hand, in pyrones the negative charge increases somewhat when oxygen is replaced by sulphur[187] and possibly by selenium. This does not, however, lead to an increase of ΔH in the above series as a result of the increasing contribution of the electrostatic interaction, probably because of the increase of the atomic radius of Y.

Egorochkin et al.[188] inferred a change in the electron-donating capacity of chalcogens in the compounds $[(C_2H_5)_3M]_2Y$ (M = Si, Ge or Sn) from the value of $\Delta\nu$(C–D) i.e. from the shift of the C–D band of deuterochloroform on complex formation. According to $\Delta\nu$ measurements, the electron-donating capacity of Y in the $[(C_2H_5)_3Si]_2Y$ series diminishes in the sequence Te > Se > S > O, which is the exact reverse of the series quoted above for chalcogen–carbon compounds. In the series with M = Ge or Sn, the general sequence in terms of decreasing electron-donating capacity, i.e. O > Te > Se > S, also differs from the series for carbon compounds. According to the authors[188], the complete or partial inversion of the electron-donating capacity series for chalcogens on passing from carbon compounds to compounds of its electronic analogues can be accounted for by the effects of the $p\pi - d\pi$ conjugation between M and Y, which leads to a decrease of the electron-donating capacity of Y. The capacity of chalcogens for $p\pi - d\pi$ conjugation with the elements of the carbon subgroup diminishes in the sequence O > S > Se > Te and the capacity of Group IV elements for such conjugation varies in the sequence Si > Ge > Sn. If this is the case, then the electron-donating capacity of oxygen linked to silicon should diminish to the greatest extent owing to the $p\pi - d\pi$ conjugation.

Table 18. The spectroscopic and thermodynamic characteristics of the hydrogen bonds formed by 2,6-di-t-butylphenol (ArOH), thiophenol, and selenophenol with pyridine[195].

Proton donor	Bond	τ_0, p.p.m.	$\Delta\tau$, p.p.m.	$K^{40°}$, (mole fraction)$^{-1}$	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
ArOH	O—H ... N	5.17	3.20	3.0	5.0	14
PhSH	S—H ... N	6.85	3.12	1.2	3.2	10
PhSeH	Se—H ... N	8.62	4.42	2.5	3.4	9

The present author believes that the decrease of the electron-donating capacity of $(R_3M)_2Y$ on replacement of, say, M = C by M = Si with Y constant can be accounted for with the aid of the concept of the $p_\pi - d_\pi$ conjugation. On the other hand, the series based on the variation of the electron-donating capacity of Y for different M proposed by Egorochkin et al.[188] and their treatment appear to be doubtful. Firstly, these series have been established only on the basis of the $\Delta\nu$(C–D), which reflect only the change in the strength of the C–D bond on complex formation and may not be correlated with the energy of the hydrogen bond (for a more detailed treatment, see below). For this reason, the basicity series can be established reliably only by measuring the thermodynamic characteristics of the hydrogen bond. Furthermore, the series proposed by Egorochkin et al.[188] conflict with other data[189,190] for hydrogen bonds involving the compounds $R_3P{=}Y$ (Y = O, S, Se or Te). The latter studies established on the basis of determinations of ΔH that the sequence based on the variation of the electron-donating capacity of chalcogens linked to phosphorus agrees fully with the corresponding series for carbon compounds, i.e. O > S > Se > Te. We may note that the effect of the $p_\pi - d_\pi$ conjugation in the P=Y bond should be greater than in the Si–Y bond, since the increase of nuclear charge from silicon to phosphorus causes a contraction of the atomic *d* orbitals of phosphorus and this leads in its turn to an improvement of the conditions for $d-p$ overlapping[191]. Thus, there are at present no adequate grounds for the assumption that the sequence based on the variation of the electron-donating capacity in the hydrogen bonds of chalcogens in their compounds with silicon is different from that in compounds with carbon or phosphorus.

The situation is different in rigid systems, such as, for example, the intramolecular hydrogen bond. We examined above studies from which it follows that, on formation of hydrogen-bonded chelates, sulphur can behave as a more effective electron donor than oxygen. However, there are insufficient data to extend this series to selenium compounds let alone tellurium compounds.

The intramolecular hydrogen bond in 3-methyl-1-phenyl-4-phenylaminomethylene-5-pyrazolone and in its thio- and seleno-analogues has been investigated by NMR[192]. The measured values of $\tau_{NH...Y}$ and J_{NH-CH} (the spin–spin interaction constants) suggest[192] that the strength of the N–H...Y (Y = O, S, or Se) intramolecular hydrogen bond, giving rise to six-membered conjugated chelate rings, increases in the sequence O < S < Se. The construction of planar models enabled the authors of the above study to conclude that the geometry of the selenium derivative is more favourable from the standpoint of the formation of a hydrogen bond than that of the oxygen and sulphur analogues. The model for selenopyrazolone demonstrates an almost linear disposition of atoms in the N–H...Se fragment and hence the most effective overlapping of the 1*s* orbital of the hydrogen atom with the pure *p* orbital of the lone electron pair of selenium. Possibly the increase of the strength of the intramolecular hydrogen bond in the sequence O < S < Se is also due to the molecular geometry, which is more favourable for the formation of the bond.

The strength of the intermolecular hydrogen bond in the cyclic dimers of 2-pyridone and its thio- and seleno-analogues increases, as expected, in the opposite sequence: O > S > Se.[193] Planar models of these complexes show that the ring strain in the dimer increases on replacement of oxygen by sulphur and even more so on its replacement by selenium.

The proton-donating capacity in the X–H...B (X = O, S, Se, or Te) hydrogen bond in chalcogen compounds has been very little studied. It has only been firmly established (see, for example, Zuika and Bankovskii[12]) that, on passing from oxygen compounds to the analogous sulphur compounds the proton-donating capacity of X–H is sharply reduced. This is associated with the increase of the overlap integral $\int_{X-H} = \psi_{1s(H)}.\psi_{np(X)}.d\tau$ and of electron density at the bridging hydrogen atom when X = O is replaced by X = S, which entails a decrease of the residual capacity for overlapping of the 1*s*(H) orbital[61,194]. Furthermore, the replacement of O by S leads to a decrease of the dipole moment of the X–H bond and hence to a decrease of the contribution of the electrostatic interaction to the overall energy of the hydrogen bond. When these explanations are extended to selenium and tellurium compounds, one may expect that the proton-donating capacity will decrease in the sequence OH > SH > SeH > TeH. However, no experimental confirmation of this hypothesis has so far been obtained. There has been only one relevant study[195] where the hydrogen bonds formed by 2,6-di-t-butylphenol, thiophenol, and selenophenol with pyridine were investigated. It was found, contrary to expectation, that selenophenol forms with pyridine an even stronger hydrogen bond than does thiophenol, although, judging from the values of τ_0, the electron density at the hydrogen atom in the X–H bond increases monotonically in the sequence OH < SH < SeH (Table 18).

The present author suggests that the observed sequence based on the variation of the proton-donating capacity, namely OH > SH < SeH, can be accounted for on the basis of the following postulates. According to Lippincot and Schroeder[196], the heat of formation of the X–H...B hydrogen bond can be represented by the sum

$$\Delta H = Q_{X-H} + Q_{X...B} + Q_{H...B},$$

where $Q_{H...B}$ is the exothermic heat of formation of the new bond, Q_{X-H} the endothermic heat of extension of the X–H bond, and $Q_{X...B}$ the endothermic heat of interelectron repulsion arising when the atoms X and B approach one another. On passing from oxygen to sulphur and to selenium, $Q_{H...B}$ falls, while $Q_{X...B}$ increases for the reasons described above. These changes reduce ΔH in the above sequence. Since the strength of the X–H chemical bond diminishes on passing from oxygen to selenium, Q_{X-H} decreases in the same direction, which may result, depending on the magnitude of the effect, in an increase of ΔH. The influence of the weakening of the X–H bond formed by the proton donor on ΔH is probably particularly important for strong ionising electron donors, such as, for example, nitrogen-containing bases, since partial or complete proton transfer

$$X{-}H \ldots N \rightleftarrows X \ldots H \ldots N \rightleftarrows X^- \ldots H{-}N^+,$$

accompanied by a significant change in the length of the X–H bond, is most probable in such systems. Whereas the change in ΔH on passing from phenol to thiophenol is probably determined mainly by the changes in $Q_{H...B}$ and $Q_{X...B}$, the influence of the low strength of the Se–H bond on ΔH becomes appreciable for selenophenol. Such joint influences of all three effects on ΔH can in fact explain why thiophenol and selenophenol form hydrogen bonds of similar strength with the same electron donor.

3. GROUP VII ELEMENTS

In early studies[197-200], the changes in electron-donating capacity in the hydrogen bonds of halogen compounds were inferred from the values of $\Delta\nu$(OH) for phenol or methanol. It was assumed that the Badger–Bauer rule[171] is valid for the O–H...Y system for any Y. Measurements of $\Delta\nu$(OH) showed that the electron-donating properties are enhanced in the sequence F < Cl < Br < I. However, analysis of the thermodynamic characteristics of hydrogen bonds of different types showed[1,201] that the Badger–Bauer rule is applicable only to a limited range of related compounds.

The data in Table 19 are completely inconsistent with the earlier conclusion concerning the sequence of the changes in the proton-accepting capacity of the covalently bound halogen. Quantities such as $-\Delta H$ and $-\Delta F$ (the free energy change) decrease in the sequence F > Cl > Br > I, while the values of $\Delta\nu$ vary in the opposite sequence. According to the literature[201,202], ΔF for the intramolecular hydrogen bond in 2,6-dihalogenophenols decreases in the sequence Cl ≥ Br > F > I. However, the results of Baker and Kaeding[201] and Richards and Walker[202], on the one hand, and West et al.,[174] on the other, are not inconsistent, since mainly steric factors influence the changes in ΔF in systems with intramolecular hydrogen bonds.

Table 19. The thermodynamic and spectroscopic characteristics of the hydrogen bonds formed by phenol with cyclohexyl halides[174].

Electron donor	$\Delta\nu$, cm^{-1}	$-\Delta H$, kcal mole^{-1}	$-\Delta F^{25°}$, kcal mole^{-1}	$-\Delta S$, e.u.
Cyclohexyl fluoride	53	3.13	1.31	6.1
Cyclohexyl chloride	66	2.21	0.87	4.5
Cyclohexyl bromide	82	2.05	0.85	4.0
Cyclohexyl iodide	86	1.72	0.82	3.0

West et al.[174] put forward a qualitative explanation of the absence of correlation between ΔH and $\Delta\nu$ in many instances. ΔH is known to reflect the total energy of the A–H...Y–R interaction, i.e. the H...Y bond strength; $\Delta\nu$ represents a measure of the weakening of the A–H bond only. Consequently, for a constant proton donor A–H, $\Delta\nu$ may be correlated with ΔH for small changes in the electron donor molecule, i.e. in R, but such correlation need not necessarily persist when Y is altered or even when the degree of hybridisation of the electrons in Y is changed.

The results of West et al.[174] were confirmed by NMR and infrared spectroscopic measurements[203] of the association constants of phenol with n-hexyl fluoride, n-butyl chloride, n-butyl bromide, and n-butyl iodide. Although there are certain quantitative discrepancies between the values of K determined by different methods, nevertheless the sequence based on the variation of the proton-accepting capacity of alkyl halides (F > Cl > Br > I) remains unchanged. The values of ΔH for the association of phenol with $C_6H_{11}F$ (0.9 kcal mole^{-1}) and $C_6H_{11}Cl$ (0.5 kcal mole^{-1}), which were determined calorimetrically[204], proved to be smaller by a factor of 3–4 than the ΔH for the same systems calculated from infrared spectroscopic data[174]. For the O–H...X (X = F or Cl) bonds, the absolute value of $\Delta H < 1$ kcal mole^{-1} should probably be regarded as too low, since a weaker proton donor (chloroform) forms with carbon tetrachloride C–H...Cl bonds having $-\Delta H \simeq 1.5$ kcal mole^{-1}.[205]

The intramolecular O–H...X (X = halogen) bonds in *o*-substituted halogenophenols and the influence of these bonds on the position of the *cis–trans* equilibrium have been studied in a number of investigations[206-210]. The values of ΔH obtained[210] show that the strength of the intramolecular hydrogen bond decreases in the sequence F (1.63) = Cl (1.63) > Br (1.53) > I (1.32) for the gas phase, and in the sequence Cl (1.62) > Br(1.57) > I (1.45) ≥ F (1.44) for cyclohexane solutions. According to Tiensung Lin and Fishman[209], the values of ΔH for the gas phase are approximately twice as large, although a similar sequence persists: Cl (3.41) > Br (3.13) > I (2.75). The behaviour of fluorine[210], which forms virtually the strongest hydrogen bond in the gas phase and the weakest in solution, is the most remarkable. According to Carlson and Fateley[210], the sequence of halogens based on the variation of their electron-donating capacity in the gas phase is consistent with the sequence which would be expected from the size and electronegativities of the halogens. On the basis of its electronegativity alone, fluorine should form a stronger bond than chlorine, but the smaller size of the fluorine atom causes some decrease in bond strength, since the OH group is unable to approach sufficiently closely for optimum overlapping of the 1*s*(H) and 2*p*(F) orbitals. In inert solvents, *o*-fluorophenol forms the least stable intramolecular hydrogen bond, which indicates the highest *trans* : *cis* ratio. The *trans*-isomer is probably stabilised in this case by the preferential formation of intermolecular hydrogen bonds, since the electron-donating capacity of fluorine is a maximum in the series of halogens.

The relative proton-donating capacities of hydrogen halides have been investigated[211-214]. It was found for solutions in aromatic hydrocarbons that the relative shift $\Delta\nu/\nu$ of the X–H bond on formation of a hydrogen bond with a standard electron donor diminishes from HF to HI.[211] The ratio of the band intensities of the bound and free H–X molecules increases in the same sequence. On this basis, it was concluded that the stability of the hydrogen-bonded complexes is determined by the acidity of HHal and that the relative band shift does not characterise the stability of this complex. A similar claim was made by workers[212] who measured the frequencies of the complexes formed by HF, HCl and HBr with dioxan. However, other results[213,214], obtained from measurements of ΔH for the hydrogen bonds between HX and benzene, carbon tetrachloride, ketones, and ethers in carbon tetrachloride solutions and in the gas phase, cast doubt on these conclusions[211,212]. It was found that the energy of the hydrogen bond formed by HX with all the electron donors enumerated above is a maximum for HF, decreasing on passing to HCl and still more on passing to HBr. For example, in the case of acetone $-\Delta H$ for HF, HCl, and HBr is 8.4, 6.1, and 5.7 kcal mole^{-1} respectively. The energy of the X–H... B hydrogen bond and the relative frequency shift were found to vary in parallel.

Thus the strength of the hydrogen bond formed by the proton donors X–H (X = F, Cl, Br, or I) with a specified acceptor decreases with increasing acidity of the hydrogen halide, which is probably due to the decrease of the residual capacity for overlapping of the 1*s*(H) orbital as the electronegativity of the halogen diminishes. It is noteworthy that, according to Shchepkin[214], the maximum change in the energy of the X–H... B bond occurs on passing from HF to HCl. When HCl is replaced by HBr, the change is much smaller. In the series of proton

donors PhXH (X = O, S, or Se) the small differences between the ΔH for the heavy atoms can probably be explained by the weakening of the X–H bond, which is said[196] to compensate to some extent the decrease in ΔH owing to the reduction of the residual capacity for overlapping of the 1*s*(H) orbital in the same direction.

Thus the electron-donating capacity of R–X and the proton-donating capacity of X–H decrease in the sequence F > Cl > Br > I, the maximum difference between these properties being observed on passing from fluorine to chlorine.

IV. CERTAIN GENERAL PROBLEMS OF THE HYDROGEN BOND

The sum total of the data discussed in previous sections makes it possible to establish certain general regularities in the variation of the proton- and electron-donating capacities in the hydrogen bonds formed by analogous compounds of Group V–VII elements. An attempt will also be made to determine wherever possible the factors which play a decisive role in the variation of the properties of the A–H...Y, X–H...B, and X–H...Y hydrogen bonds (where A–H and B are standard proton and electron donors and X and Y are a series of elements belonging to a single Group or Period).

For the A–H...Y hydrogen bonds, the electron-donating capacity of Y, belonging to the given Group, diminishes on passing to heavier elements: N > P > As > Sb; O > S > Se > Te; F > Cl > Br > I. The greatest differences between the electron-donating capacities are observed on passing from the elements in the Second Period to those in the Third Period, i.e. between nitrogen and phosphorus, between oxygen and sulphur, and between fluorine and chlorine, while for heavier elements the differences are much less pronounced. We may note that even elements such as antimony, tellurium, and iodine, which are of the metallic or semimetallic type, are capable of forming hydrogen bonds as electron donors. Proton-accepting capacity can probably be regarded as virtually the exclusive property of the free electron pair and there is at present no reason to deny the possession of this property by still heavier atoms such as those of bismuth, polonium, and astatine.

According to modern ideas[10,181], the main contribution to the formation of the hydrogen bond comes from the electrostatic interaction, the repulsion of electron clouds, and the redistribution of electron density. The latter involves the overlapping of the 1*s*(H) and *np*(Y) orbitals and charge transfer from the highest occupied orbital of the proton acceptor Y to the antibonding σ orbital of the proton donor A–H. The data obtained for the decrease of the electron-donating capacity in Groups V–VII on passing to heavier elements suggest that the main contribution to the hydrogen bond energy is made by the overlapping of the 1*s*(H) and *np*(Y) orbitals. With increase of n, p electrons become more diffuse and their orbital density diminishes; together with the interelectron repulsion, which increases in the same direction, this causes a decrease of the capacity for overlapping of the *np*(Y) orbital. From the standpoint of the model of charge-transfer complexes, the opposite behaviour would be observed—the electron-donating capacity of Y should increase with increase of n, since this entails a diminution of the ionisation potential.

We may note that the role of charge transfer in the hydrogen bond is the most controversial problem. This model is attractive, because it involves the inclusion of hydrogen-bonded complexes in the general class of donor–acceptor complexes. However, the correlation between the ionisation potentials of Y and the thermodynamic characteristics of association by hydrogen bonding is limited[1]. The most important experimental argument against the charge-transfer model of the hydrogen bond is the absence of the charge-transfer band from the spectra of hydrogen-bonded complexes[215]. Analysis of the infrared spectra with the aid of the vibronic theory[178,216], based on Mulliken's ideas[180], also showed[166] that charge transfer does not play a decisive role in the formation of the hydrogen bond by the elements of the same Group as electron donors.

As already stated, the effect of charge transfer may reduce merely to a decrease of the difference between the heats of association of neighbouring members of the Group as the ionisation potential is reduced. The increase of the polarisability of the electrons in Y with increase of n, resulting in an increase of the contribution of dispersion interaction, may play the same role.

The fastest decrease of proton-accepting capacity with increasing atomic number has been observed in a series of electron donors belonging to Group V. Chojnowski[166] explains this by the fact that the greatest differences between the hybridisations of the free electron pair orbital are characteristic of Group V elements. This follows from a comparison of the valence angles in the corresponding alkyl derivatives: 109° for $(CH_3)_3N$, 100° for $(CH_3)_3P$, and 96°C for $(CH_3)_3As$ in Group V and 111° for $(CH_3)_2O$ and 105°C for $(CH_3)_2S$ in Group VI. These data show that the increase of the amount of s character of the free electron pair orbital, resulting in a decrease of its capacity for overlapping[217,218], is faster in Group V than in Group VI. If one assumes by analogy that the amount of s character increases at the lowest rate in Group VII, one can understand the small change in electron-donating capacity on passing from chlorine to bromine and iodine.

We shall now consider how the electron-donating capacity changes in the A–H...Y hydrogen bonds for Y belonging to different Groups in the same Period. It was established previously[1] that the electron-donating capacity of the elements in the Second Period decreases in the sequence N > O > F, i.e. with increase of the electronegativity of Y. The data in Tables 13–15 and 19 suggest that this tendency in the variation of the electron-donating capacity is maintained in the Third, Fourth, and possibly Fifth Periods (P > S > Cl; As > Se > Br; Sb > Te > I), although the differences for neighbouring numbers of the series gradually diminish with increasing number of the Period. Calculations of the hydrogen bond energy[27] and the H...Y bond populations[219] showed, in agreement with experimental data, that the electron-donating capacity of Y decreases in the sequences P > S > Cl and Se > Br.

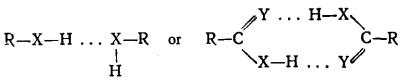
Thus the available data suggest that the electron-donating capacity of Group V–VII elements in the same Period decreases with increasing electronegativity, in contrast to the series of electron donors in a single Group. Consequently the electrostatic interaction is not of decisive importance in the formation of hydrogen bonds even with "hard" bases such as oxygen and fluorine compounds. The proton-accepting capacity of the elements in a single Period is probably determined by the redistribution of charge between the molecular fragments of the complex AH...Y owing to the overlapping of the 1*s*(H) and *np*(Y) orbitals and as a result of charge transfer from the *np*(Y) orbital of the proton acceptor to the antibonding σ orbital of the A–H bond of the proton donor. On passing from nitrogen to fluorine, from phosphorus to chlorine, etc., the number of free electron pairs of the atom Y increases,

which leads to an intensification of the interelectron repulsion [176] in A...Y and impairment of the conditions for the overlapping of the 1*s*(H) and *np*(Y) orbitals. Furthermore, the increase of the ionisation potential in the same direction hinders charge transfer to the antibonding σ orbital of the A–H bond. The joint operation of the above factors can account for the observed decrease of the electron-donating capacity within the limits of the same Period on passing to heavier elements.

We shall now consider how the proton-donating capacity changes in the X–H...B hydrogen bond, although, as we have seen, there are very few literature data for the elements in the Third, Fourth, and Fifth Periods. Nevertheless, one can assume that, for elements of the same Group or Period, the following series based on decreasing proton-donating capacity are valid: NH > PH, OH > SH ≃ SeH, FH > ClH > BrH > IH, FH > OH > NH, and ClH > SH > PH. [27]

The proton-donating capacity of the XH group is known [2] to be determined mainly by the tendency of the H atom in this group to accept electrons from the B atom, using the residual capacity for overlapping of the 1*s*(H) orbital. This capacity should increase with decrease of the overlap integral of the X–H bond [60], i.e. with increase of the degree of dissociation of the hydrogen atom as a proton. With increase of the electronegativity of the X atom, the overlap integral for the X–H bond diminishes, which entails an increase of the proton-donating capacity of the X–H group. Furthermore, the dipole moment of the X–H bond and hence also the contribution of the electrostatic interaction to the hydrogen bond energy increase with increasing electronegativity of X. These factors are in fact responsible for the increase of the proton-donating capacity of X–H on passing to heavier elements in the Period and to lighter elements in the Group. It is noteworthy that, within the limits of the same Period, the acidity and proton-donating capacity of X–H are the same, since the X–H bond energy and the degree of dissociation of the hydrogen atom as a proton vary in opposition. On the other hand, within the limits of a single Group, the bond energy and the degree of dissociation vary in parallel, which gives rise to the inverse relation between acidity and proton-donating capacity.

We shall now consider how the properties of the hydrogen bond are affected by the simultaneous variation of the proton- and electron-donating capacities of the interacting molecules. Such a situation arises in self-association processes:



when the substituent is altered. Electron-accepting substituents, for example, increase the proton-donating capacity of the X–H group but reduce the electron-donating capacity of X or Y. The overall effect of the substituent will depend on the relative contributions of the electron donor and proton donor to the hydrogen bond energy. Three cases are possible: (a) the contribution of the electron donor is greater than that of the proton donor and the introduction of electron-donating substituents strengthens the bond; (b) the contribution of the proton donor plays a decisive role and electron-accepting substituents strengthen the hydrogen bond; (c) the increase (decrease) of the proton-donating capacity of the X–H group is compensated by the decrease (increase) of the electron-donating capacity of X or Y and the strength of the hydrogen bond should not then depend on the nature of the substituent.

Analysis of the experimental data enabled the author of this review to put forward certain hypotheses of a general type [85]. Thus it has been established that the strength of hydrogen bonds in self-associated species of substituted anilines increases following the introduction of electron-donating substituents [220]: the tendency of mercaptans towards self-association is more pronounced than that of thiophenol [15]; the degree of self-association of phenols increases in the sequence *p*-chlorophenol < *p*-fluorophenol < *p*-cresol [221] and the stability of the self-associated species increases on passing from ethyl alcohol to t-butyl alcohol [94]. All these data lead to the conclusion that, in series of compounds forming hydrogen bonds of the type NH...N, SH...S, OH...O, and probably in general "homoquantum" bonds of the type X–H...X′(where X and X′ are atoms of elements belonging to the same Period), the variation of the hydrogen bond strength is determined mainly by the variation of the properties of the electron donor.

On the other hand, in series of compounds associated via "heteroquantum" bonds of the type X–H...Y (where X and Y are elements belonging to different Periods), the variation of the stability of the associated species is presumably determined by the variation of the properties of the atom whose electrons, involved in the formation of the hydrogen bond, are characterised by a larger principal quantum number. Thus the variation of ΔH for the S–H...O bond should be determined by the variation of the proton-donating capacity of the SH group and for the NH...P bond by the variation of the electron-donating properties of the phosphorus atom under the influence of substituents. The latter hypothesis explains the type of influence of substituents on the stability of self-associated species of thiobenzoic acids [85], the ratio of the quantities ρ [Eqns. (1) and (2)] for the association of thiophenols with acetophenones [52], and the shift of the thiol–thione equilibrium [88] under the influence of substituents.

Since the influence of substituents reduces the electronic polarisation of the reaction centre of the molecule, an explanation of the essential physical features of the empirical rule which has been formulated [85] is provided by calculations, involving complete neglect of differential overlapping (CNDO/2), of the charge shifts [222] in the molecular fragments of the $HSH...OH_2$ and $HOH...SH_2$ complexes [195]. These complexes provide one of the simplest examples of "heteroquantum" hydrogen bonds. It was found that the charge shift in the H_2O molecule functioning as either an electron or proton donor is zero or many times smaller than the charge shift in the H_2S molecule. This can be accounted for by the fact that, on passing from oxygen to sulphur, the deformability and polarisability of the electron clouds increase. The above results show that, on formation of the "heteroquantum" hydrogen bonds SH...O and OH...S, the maximum charge shift occurs precisely in the fragments of the complex where a change in properties is stated [85] to have a decisive influence on the change in bond energy. Consequently the greater sensitivity of the energy of a "heteroquantum" hydrogen bond to changes in the properties of the atom with the higher principal quantum number of the valence electrons can be explained by the fact that the maximum charge shift on formation of the hydrogen-bonded complex occurs in the molecular fragment with this atom.

REFERENCES

1. G.C. Pimentel and A.L. McClellan, "The Hydrogen Bond" (Translated into Russian), Izd. Mir, Moscow, 1964.
2. Symposium, "Vodorodnaya Svyaz'" (The Hydrogen Bond), Izd. Nauka, Moscow, 1964.
3. R. Foster and C.A. Fyfe, Progr. Nuclear Magn. Resonance, 4, 1 (1969).
4. J.C. Davis and K.K. Deb, Adv. Magn. Resonance, 4, 201 (1970).
5. A.I. Brodskii, V.D. Pokhodenko, and V.S. Kuts, Uspekhi Khim., 39, 753 (1970) [Russ. Chem. Rev., No. 5 (1970)].
6. A.S.N. Murthy and C.N.R. Rao, Appl. Spectrosc. Rev., 2, 1 (1968).
7. H. Ratajczak and W.J. Orville-Thomas, J. Mol. Struct., 1, 449 (1968).
8. S. Bratoz, Adv. Quant. Chem., 3, 209 (1967).
9. A.S.N. Murthy and C.N.R. Rao, J. Mol. Struct., 6, 253 (1970).
10. P.A. Kollman and L.C. Allen, Chem. Rev., 72, 283 (1972).
11. N.D. Sokolov, Zhur. Vses. Khim. Obshch., 17, 299 (1972).
12. I.V. Zuika and Yu.A. Bankovskii, Uspekhi Khim., 42, 39 (1973) [Russ. Chem. Rev., No. 1 (1973)].
13. S.H. Marcus and S.J. Miller, J. Phys. Chem., 68, 331 (1964).
14. S.H. Marcus and S.J. Miller, J. Phys. Chem., 73, 453 (1969).
15. S.H. Marcus and S.J. Miller, J. Amer. Chem. Soc., 88, 3719 (1966).
16. S.J. Hu and S.J. Miller, Org. Magn. Resonance, 5, 197 (1973).
17. S. Signh and C.N.R. Rao, J. Phys. Chem., 71, 1074 (1967).
18. M.M. Rousselot and M.I. Lekomte, Compt. rend., (C), 262, 26 (1966).
19. A.P. Kilimov, M.A. Svechnikova, B.M. Gladshtein, and B.L. Zakharov, Zhur. Obshch. Khim., 37, 768 (1967).
20. J.E. Lowder, J. Quant. Spectr. Radiat. Transfer, 10, 1085 (1970).
21. O.P. Yablonskii, N.M. Rodionova, and L.F. Lapuka, Zhur. Prikl. Spektrosk., 19, 654 (1973).
22. O.P. Yablonskii, N.M. Rodionova, and L.F. Lapuka, Zhur. Prikl. Spektrosk., 19, 750 (1973).
23. F.D. Mamedov and M.A. Salimov, Izv. Akad. Nauk Azerb. SSR, 104 (1973).
24. C.R. Kanekar, G. Govil, C.L. Knetropal, and H.H. Dhinqru, Proc. Indian Acad. Sci., 65A, 265 (1967).
25. W.S. Fyfe, J. Chem. Phys., 21, 2 (1953).
26. J.R. Sabin, J. Chem. Phys., 54, 4675 (1971).
27. W.C. Topp and L.C. Allen, J. Amer. Chem. Soc., 96, 5291 (1974).
28. R.B. Alencastro and C. Sandorfy, Canad. J. Chem., 50, 3594 (1972).
29. G. Geiseler, H. Seidel, and J. Fruwert, Spectrochim. Acta, 29A, 1385 (1973).
30. K. Morokuma and L. Pedersen, J. Chem. Phys., 48, 3275 (1968).
31. J.R. Sabin, J. Amer. Chem. Soc., 93, 3613 (1971).
32. P.A. Kollman and L.C. Allen, J. Amer. Chem. Soc., 92, 753 (1970).
33. P.A. Kollman and L.C. Allen, J. Chem. Phys., 51, 3286 (1969).
34. P.A. Kollman and L.C. Allen, J. Chem. Phys., 52, 5085 (1970).
35. M. Eigen, Discuss. Faraday Soc., 39, 7 (1965).
36. R.L. Scott, J. Phys. Chem., 75, 3843 (1971).
37. R. Mathur, E.D. Becker, R.B. Bradley, and N.C. Li, J. Phys. Chem., 67, 2190 (1963).
38. R. Mathur, S.M. Wang, and N.C. Li, J. Phys. Chem., 68, 2140 (1964).
39. V.K. Pogorelyi and I.P. Gragerov, Dokl. Akad. Nauk SSSR, 186, 610 (1969).
40. S.J. Hu, E. Goldberg, and S.L. Miller, Org. Magn. Resonance, 4, 683 (1972).
41. N. Muller and R.C. Reiter, J. Chem. Phys., 42, 3265 (1965).
42. G.R. Willey and S.J. Miller, J. Amer. Chem. Soc., 94, 3287 (1972).
43. V.K. Pogorelyi, Candidate's Thesis, Institute of Physical Chemistry, Kiev, 1969.
44. S. Singh, A.S.N. Murthy, and C.N.R. Rao, Trans. Faraday Soc., 62, 1056 (1966).
45. S. Mukherjee, S.R. Palit, and S.K. De, J. Phys. Chem., 74, 1389 (1970).
46. J.G. David and H.F. Hallam, Trans. Faraday Soc., 60, 2013 (1964).
47. G.B. Barlin and D.D. Perrin, Quart. Rev., 20, 75 (1966).
48. V.K. Pogorelyi and I.I. Kukhtenko, Teor. Eksper. Khim., 8, 253 (1972).
49. I.M. Ginzburg, Optika i Spektrosk., 17, 57 (1964).
50. K. Müller, Org. Magn. Resonance, 3, 331 (1971).
51. V. Palm, Uspekhi. Khim., 30, 1069 (1961) [Russ. Chem. Rev., No. 9 (1961)].
52. V.K. Pogorelyi and I.I. Kukhtenko, Teor. Eksper. Khim., 8, 400 (1973).
53. G.V. Sandul, V.S. Kuts, and V.D. Pokhodenko, Teor. Eksper. Khim., 8, 349 (1972).
54. V.K. Pogorelyi, V.P. Prokopenko, and I.P. Gragerov, Teor. Eksper. Khim., 10, 399 (1974).
55. V.K. Pogorelyi and I.P. Gragerov, Uspekhi. Khim., 39, 1856 (1970) [Russ. Chem. Rev., No. 10 (1970)].
56. J. Schneider, J. Chem. Phys., 23, 26 (1953).
57. R.S. Drago, J. Amer. Chem. Soc., 85, 3125 (1963).
58. A.E. Lutskii and E.I. Goncharova, Ukrain. Khim. Zhur., 38, 1223 (1972).
59. V.K. Pogorelyi, V.P. Prokopenko, and I.P. Gragerov, Teor. Eksper. Khim., 11, 597 (1975).
60. A.E. Lutskii, Zhur. Obshch. Khim., 32, 4099 (1962).
61. A.E. Lutskii, Teor. Eksper. Khim., 1, 815 (1965).
62. A.E. Lutskii, A.I. Mitichkin, and G.I. Sheremet'eva, Dokl. Akad. Nauk SSSR, 214, 381 (1974).
63. J.G. David and H.F. Hallam, Spectrochim. Acta, 21, 841 (1965).
64. M. Lambroso and R. Passerini, Bull. Soc. Chim. France, 311 (1957).
65. A.E. Lutskii, A.K. Kul'chitskaya, E.M. Obukhova, and G.I. Sheremet'eva, Zhur. Obshch. Khim., 36, 1577 (1966).
66. I.M. Ginzburg and A.A. Loginova, Dokl. Akad. Nauk SSSR, 156, 1382 (1964).
67. E.I. Guliev and B.I. Sultanov, Dokl. Akad. Nauk Azerb. SSR, 28, 29 (1972).
68. M. Hirota and R. Hashi, Tetrahedron, 25, 5953 (1969).
69. F. Duus, E.B. Pedersen, and S.O. Lawesson, Tetrahedron, 25, 5703 (1969).
70. T. Kobayashi, A. Yamashita, Y. Furuya, R. Horie, and M. Hirota, Bull. Chem. Soc. Japan, 45, 1494 (1972).

71. N.Mori, S.Kaido, K.Suzuki, M.Nakamura, and Y.Tsuzuki, Bull.Chem.Soc.Japan, 44, 1858 (1971).
72. D.Plant, D.S.Tarbell, and C.Whiteman, J.Amer. Chem.Soc., 77, 1572 (1955).
73. P.J.Krueger, Tetrahedron, 26, 4753 (1970).
74. W.R.Snyder, H.D.Schreiber, and J.N.Spencer, Spectrochim.Acta, 29A, 1225 (1973).
75. J.N.Spencer, L.Casey, J.Buckfelder, and H.D.Schreiber, J.Phys.Chem., 78, 1415 (1974).
76. A.E.Lutskii, Teor.Eksper.Khim., 7, 95 (1971).
77. R.Mecke and H.Spiesecke, Chem.Ber., 89, 1110 (1956).
78. N.Sheppard, Trans.Faraday Soc., 45, 693 (1949).
79. M.Cefola, P.S.Simon, P.S.Gentile, and A.V.Celiano, Talanta, 9, 537 (1962).
80. I.M.Ginzburg and A.A.Loginova, Optika i Spektrosk., 20, 241 (1966).
81. A.S.N.Murthy, C.N.R.Rao, B.D.N.Rao, and P.Venkateswarlu, Trans.Faraday Soc., 58, 855 (1962).
82. L.I.Gur'eva and V.I.Dulova, Zhur.Fiz.Khim., 46, 831 (1972) [Russ.J.Phys.Chem., No.4 (1972)].
83. R.B.Alencastro and C.Sandorfy, Canad.J.Chem., 51, 1443 (1973).
84. V.K.Pogorelyi, Teor.Eksper.Khim., 7, 841 (1971).
85. V.K.Pogorelyi, Dokl.Akad.Nauk SSSR, 204, 110 (1972).
86. P.K.Glasoe, S.Hallock, M.Hove, and J.M.Duke, Spectrochim.Acta, 27A, 2309 (1971).
87. S.T.Ioffe, Yu.N.Sheinker, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1561 (1960).
88. S.T.Ioffe, Yu.N.Sheinker, and M.I.Kabachnik, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1571 (1960).
89. G.Allen and R.O.Colclough, J.Chem.Soc., 3912 (1957).
90. M.I.Kabachnik and T.A.Mastrjukova, Tetrahedron, 9, 10 (1960).
91. V.K.Pogorelyi, I.I.Kukhtenko, and T.A.Mastryukova, Dokl.Akad.Nauk SSSR, 214, 358 (1974).
92. F.Lippert, Ber.Bunsenges phys.Chem., 67, 267 (1963).
93. C.M.Huggins, G.C.Pimentel, and J.M.Shoolery, J.Phys.Chem., 60, 1311 (1956).
94. G.Feeney and S.M.Walker, J.Chem.Soc., 1148 (1966).
95. A.Menefee, D.Alford, and C.Scott, J.Chem.Soc., 25, 370 (1956).
96. L.J.Bellamy, "The Infrared Spectra of Complex Molecules", London, 1958.
97. E.V.Rakitina and N.T.Loseva, Dokl.Akad.Nauk Tadzh.SSR, 13, 28 (1970).
98. E.M.Popov, Candidate's Thesis, Institute of Organoelement Compounds, Moscow, 1958.
99. E.M.Popov, M.I.Kabachnik, and L.S.Mayants, Uspekhi.Khim., 30, 846 (1961) [Russ.Chem.Rev., No.7 (1961)].
100. R.A.Bulgakova and R.R.Shagidullin, Izv.Akad. Nauk SSSR, Ser.Khim., 672 (1968).
101. R.R.Shagidullin, I.P.Lipatova, L.I.Vachugova, and R.A.Cherkasov, Izv.Akad.Nauk SSSR, Ser. Khim., 847 (1972).
102. R.R.Shagidullin, I.P.Lipatova, O.A.Raevskii, and L.I.Vachugova, Izv.Akad.Nauk SSSR, Ser.Khim., 541 (1973).
103. V.K.Pogorelyi, I.I.Kukhtenko, and T.F.Divnich, Teor.Eksper.Khim., 11, 242 (1975).
104. T.A.Mastryukova, Doctoral Thesis, Institute of Organoelement Compounds, Moscow, 1967.
105. M.I.Kabachnik, Dokl.Akad.Nauk SSSR, 110, 393 (1956).
106. T.A.Mastryukova and M.I.Kabachnik, Uspekhi. Khim., 38, 1751 (1969) [Russ.Chem.Rev., No.10 (1969)].
107. H.Marsmann, L.C.D.Gruenweghe, L.J.Schaad, and J.R.Van Wazer, J.Amer.Chem.Soc., 92, 6107 (1970).
108. V.K.Pogorelyi and I.I.Kukhtenko, "Tezisy XII Ukrainskoi Respublikanskoi Konferentsii po Organicheskoi Khimii, Uzhgorod, 1974" (Abstract of Reports at the XIIth Ukrainian Republic Conference on Organic Chemistry, Uzhgorod, 1974), p.109.
109. M.Eigen and L.de Maeyer, "Rates and Mechanisms of Reactions", New York, 1963.
110. N.D.Sokolov, Dokl.Akad.Nauk SSSR, 60, 825 (1948).
111. A.I.Brodskii, Izv.Akad.Nauk SSSR, Otd.Khim. Nauk, 3 (1949).
112. A.I.Brodskii, Dokl.Akad.Nauk SSSR, 33, 847 (1953).
113. D.G.Knorre and N.M.Emanuel', Uspekhi.Khim., 24, 275 (1955).
114. A.I.Brodskii, Symposium, "Vodorodnaya Svyaz'" (The Hydrogen Bond), Izd.Nauka, Moscow, 1964.
115. N.D.Sokolov, Uspekhi Fiz.Nauk, 57, 205 (1955).
116. E.Grunwald, Progr.Phys.Org.Chem., 3, 307 (1965).
117. E.A.Pshenichnov and N.D.Sokolov, Dokl.Akad. Nauk SSSR, 137, 352 (1961).
118. E.A.Pshenichnov and N.D.Sokolov, Inter.J. Quantum Chem., 1, 855 (1967).
119. G.V.Sandul, V.S.Kuts, and V.D.Pokhodenko, Teor. Eksper.Khim., 8, 340 (1972).
120. V.K.Pogorelyi, V.P.Prokopenko, and I.P.Gragerov Teor.Eksper.Khim., 8, 253 (1972).
121. V.P.Prokopenko, V.K.Pogorelyi, and I.P.Gragerov, Zhur.Org.Khim., 11, 1802 (1975).
122. J.F.Whidby and D.E.Leiden, J.Phys.Chem., 74, 202 (1970).
123. P.C.Jocelyn, "Biochemistry of the SH-group", Acad.Press, New York, 1972.
124. I.P.Gragerov, V.K.Pogorelyi, and A.I.Brodskii, Dokl.Akad.Nauk SSSR, 178, 880 (1968).
125. I.P.Gragerov and V.K.Pogorelyi, Dokl.Akad.Nauk SSSR, 185, 1052 (1969).
126. H.Lippert and T.Prigge, Annalen, 659, 81 (1962).
127. N.Mori, Y.Takahashi, and Y.Tsuzuki, Bull.Chem. Soc.Japan, 40, 2720 (1967).
128. R.W.Taft, D.Gurka, and P.R.Schleyer, J.Amer. Chem.Soc., 91, 4801 (1969).
129. T.Gramstad and W.J.Fuglevik, Acta Chem.Scand., 16, 2368 (1962).
130. R.Arnold, G.Klose, P.H.Thomas, and E.Uhlemann, Tetrahedron, 25, 2957 (1969).
131. S.Mukherjee, A.K.Ghosh, S.K.Palit, and S.K.De, J.Indian Chem.Soc., 47, 1053 (1970).
132. T.M.Barakat, J.Nelson, S.M.Nelson, and A.D.E.Pullin, Trans.Faraday Soc., 65, 41 (1969).
133. M.Goldstein, C.B.Mullins, and H.A.Willis, J. Chem.Soc.(B), 321 (1970).
134. A.D.Sherry and K.F.Purcell, J.Amer.Chem.Soc., 94, 1853 (1972).
135. M.O.Bulanin, G.S.Denisov, and R.A.Pushkina, Optika i Spektrosk., 6, 754 (1959).
136. H.L.Liao and D.E.Martire, J.Amer.Chem.Soc., 96, 2058 (1974).
137. G.C.Vogel and R.S.Drago, J.Amer.Chem.Soc., 92, 5347 (1970).

138. R.S. Drago, G.C. Vogel, and T.E. Needham, J. Amer. Chem. Soc., 93, 6014 (1971).
139. R.S. Drago and T.D. Epley, J. Amer. Chem. Soc., 91, 2883 (1969).
140. K.F. Purcell, J.A. Stikeleather, and S.D. Brunk, J. Amer. Chem. Soc., 91, 4019 (1969).
141. R.S. Drago and B.B. Wayland, J. Amer. Chem. Soc., 87, 3571 (1965).
142. R.G. Pearson, J. Chem. Educ., U5, 581, 643 (1968).
143. J.P. Sheridan, D.E. Martire, and Y.B. Tewari, J. Amer. Chem. Soc., 94, 3294 (1972).
144. W.G. Paterson and D.M. Cameron, Canad. J. Chem., 41, 198 (1963).
145. C.J. Creswell and A.L. Allerd, J. Amer. Chem. Soc., 85, 1723 (1963).
146. R.E. Kagarise, Spectrochim. Acta, 19, 629 (1963).
147. A.N. Campbell and E.M. Katzmark, Canad. J. Chem., 44, 917 (1966).
148. R.S. Mulliken and W.B. Person, "Molecular Complexes", Wiley-Interscience, New York, 1969.
149. J. Homer and M. Cooke, J. Amer. Chem. Soc., 91, 773, 777, 1984, 2862 (1969).
150. M.D. Johnston, F.P. Gasparro, and J.D. Kuntz, J. Amer. Chem. Soc., 91, 5715 (1969).
151. G.R. Wiley and S.J. Miller, J. Amer. Chem. Soc., 94, 3287 (1972).
152. K.W. Jolley, L.M. Hughes, and I.D. Wotson, Austr. J. Chem., 27, 287 (1974).
153. L.M. Epshtein and A.N. Zhdanova, Izv. Akad. Nauk SSSR, Ser. Khim., 87 (1974).
154. O. Foss, "Organic Sulphur Compounds", (Edited by C.I. Kharach), Oxford, 1960, Vol. 1, p. 70.
155. U. Dabrowska and J. Dabrowski, Adv. Mol. Relax. Processes, 6, 81 (1973).
156. S. Mukherjee, S.K. De, and S.R. Palit, Indian J. Chem., 11, 1011 (1973).
157. P.G.F. Griffiths, G.D. Morgan, and B. Ellis, Spectrochim. Acta, 28A, 1899 (1972).
158. A.D. Sherry and K.F. Purcell, J. Amer. Chem. Soc., 94, 1848 (1972).
159. R.R. Shagidullin, I.P. Lipatova, L.I. Vachugova, and S.A. Samartseva, Dokl. Akad. Nauk SSSR, 202, 617 (1972).
160. R.R. Shagidullin, S.V. Izosimova, and I.A. Lamanova, Izv. Akad. Nauk SSSR, Ser. Khim., 2778 (1973).
161. W. Walter and H.P. Kubersky, Annalen, 821 (1973).
162. J.P. Chesick and J. Donohue, Acta Cryst., 27B, 1441 (1971).
163. B. Ellis and P.J.F. Griffiths, Spectrochim. Acta, 22, 2005 (1966).
164. K.R. Bhaskar, R.K. Gosavi, and C.N.R. Rao, Trans. Faraday Soc., 62, 29 (1966).
165. J. Chojnowski, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 18, 309 (1970).
166. J. Chojnowski, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 18, 317 (1970).
167. E.M. Arnett, Progr. Phys. Org. Chem., 1, 223 (1963).
168. H.A. Bent, Chem. Rev., 68, 587 (1968).
169. J.H. Gibbs, J. Chem. Phys., 22, 1460 (1954).
170. D. Gurka and R.W. Taft, J. Amer. Chem. Soc., 91, 4794 (1969).
171. R.M. Badger and S.H. Bauer, J. Chem. Phys., 5, 839 (1937).
172. B. Silver and Z. Luz, J. Amer. Chem. Soc., 83, 786 (1961).
173. E. Grunwald and M. Cocivera, J. Phys. Chem., 68, 3234 (1964).
174. R. West, D.L. Powell, L.S. Wheatley, M.K. Lee, and P.R. Schleyer, J. Amer. Chem. Soc., 84, 3221 (1962).
175. R. West, D.L. Powell, M.K. Lee, and L.S. Wheatley, J. Amer. Chem. Soc., 86, 3227 (1964).
176. A.E. Lutskii, L.P. Batrakova, and L.A. Fedotova, Zhur. Obshch. Khim., 42, 1820 (1972).
177. J. Chojnowski and W.W. Brandt, J. Amer. Chem. Soc., 90, 1384 (1968).
178. H.B. Friedrich and W.B. Person, J. Chem. Phys., 44, 2161 (1966).
179. R.S. Mulliken and W.B. Person, Ann. Rev. Phys. Chem., 13, 107 (1962).
180. R.S. Mulliken, J. Chem. Phys., 61, 20 (1963).
181. F.B. Duijneveldt and J.N. Murrell, J. Chem. Phys., 46, 1759 (1967).
182. V.K. Pogorelyi, I.I. Kukhtenko, and A.E. Lutskii, Teor. Eksper. Khim., 10, 824 (1974).
183. E. Osawa, K. Kitamura, and Z. Yoshida, J. Amer. Chem. Soc., 89, 3814 (1967).
184. A.I. Tolmachev, L.V. Papp, E.V. Ryl'tsev, and Yu.P. Egorov, Zhur. Obshch. Khim., 44, 2747 (1974).
185. V.K. Pogorelyi, I.I. Kukhtenko, and A.I. Tolmachev, Teor. Eksper. Khim., 11, 619 (1975).
186. E.N. Gur'yanova, Uspekhi. Khim., 37, 1981 (1968) [Russ. Chem. Rev., No. 11 (1968)].
187. N. Brown and P. Bladon, Spectrochim. Acta, 21, 1277 (1965).
188. A.I. Egorochkin, M.N. Bochkarev, N.S. Vyazankin, S.E. Skobeleva, and S. Ya. Khoriev, Dokl. Akad. Nauk SSSR, 198, 96 (1971).
189. E.V. Ryl'tsev, I.E. Boldeskul, A.F. Pavlenko, Yu.P. Egorov, and V.P. Akkerman, Zhur. Prikl. Spektrosk., 16, 512 (1972).
190. R.R. Shagidullin, I.P. Lipatova, I.A. Nuretdinov, and S.A. Samartseva, Dokl. Akad. Nauk SSSR, 211, 1363 (1973).
191. D.P. Craig, A. Maccoll, R.S. Nyholm, L.E. Orgel, and L.E. Sutton, J. Chem. Soc., 332 (1954).
192. L.N. Kurkovskaya, N.N. Shapet'ko, I. Ya. Kvitko, and Yu.N. Koshelev, Zhur. Org. Khim., 8, 215 (1972).
193. M.H. Krackov, C.N. Lee, and H.G. Maunter, J. Amer. Chem. Soc., 87, 892 (1965).
194. C. Cannon, Spectrochim. Acta, 10, 341 (1958).
195. V.K. Pogorelyi, "Materialy XI Mendeleevskogo S'ezda, Sekstiya Fizicheskaya Khimiya" (Proceedings of the XIth Mendeleev Congress. The Physical Chemistry Section), Izd. Nauka, Alma-Ata, 1975, p. 77.
196. E.R. Lippincot and R. Schroeder, J. Chem. Phys., 23, 1099 (1955).
197. G.J. Korinek and W.G. Schneider, Canad. J. Chem., 35, 1157 (1957).
198. M.L. Josien and P. Dizabo, Bull. Soc. chim. France, 188 (1958).
199. P.R. Schleyer and R. West, J. Amer. Chem. Soc., 81, 3164 (1959).
200. E.D. Becker, Spectrochim. Acta, 17, 436 (1961).
201. A.W. Baker and W.W. Kaeding, J. Amer. Chem. Soc., 81, 5904 (1959).
202. J.H. Richards and S. Walker, Trans. Faraday Soc., 57, 412 (1961).
203. W.W. Brandt and J. Chojnowski, Spectrochim. Acta, 25A, 1639 (1969).
204. T.D. Epley and R.S. Drago, J. Amer. Chem. Soc., 89, 5770 (1967).

205. T. Gramstad and Q. Mundheim, Spectrochim. Acta, **28A**, 1405 (1972).
206. D. A. Jones and I. G. Wilkinson, Chem. Ind. (London), 661 (1960).
207. E. A. Allan and L. W. Reeves, J. Phys. Chem., 66, 613 (1962); 67, 591 (1963).
208. A. W. Baker and A. T. Schulgin, Canad. J. Chem., **43**, 650 (1965).
209. Tiensung Lin and E. Fishman, Spectrochim. Acta, **23A**, 491 (1967).
210. G. L. Carlson and W. G. Fateley, J. Phys. Chem., 76, 1553 (1972).
211. J. Lascombe and M. L. Josien, J. Chim. Phys., 54, 761 (1957).
212. P. Grange and I. Lascombe, J. Chim. Phys., 60, 1119 (1963).
213. D. N. Shchepkin, Optika i Spektrosk., 19, 1709 (1965).
214. D. N. Shchepkin, Teor. Eksper. Khim., 2, 276 (1966).
215. U. Ientschura and E. Lippert, Z. phys. Chem. (Frankfurt), 75, 88 (1971).
216. E. E. Ferguson and F. A. Matsen, J. Amer. Chem. Soc., 82, 3268 (1960).
217. M. A. Bent, J. Chem. Educ., **37**, 616 (1960).
218. J. Schneider, J. Chem. Phys., 23, 26 (1953).
219. A. E. Lutskii and T. N. Marchenko, Teor. Eksper. Khim., 10, 341 (1974).
220. G. V. Sandul, V. S. Kuts, and V. D. Pokhodenko, Teor. Eksper. Khim., 7, 658 (1971).
221. V. S. Griffiths and G. Socrates, J. Mol. Spectroscopy, **21**, 302 (1966).
222. P. A. Kollman and L. C. Allen, J. Amer. Chem. Soc., 93, 4991 (1971).

Pisarzhevskii Institute of Physical Chemistry,

Academy of Sciences of Ukrainian SSR, Kiev