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Electronic Spectroscopy of Charge-transfer Complexes as a Method for the Investigation of Intramolecular Interactions in Organic and Organoelemental Compounds

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The application of electronic absorption and emission spectroscopy of intermolecular donor-acceptor complexes (charge-transfer complexes) in the study of intramolecular effects of substituents in organic and organoelemental compounds is considered.

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I. INTRODUCTION

When donor (D) and acceptor (A) molecules interact with partial transfer of electron density, a donor–acceptor complex [a charge-transfer complex (CTC)] is formed:

$$D+A \rightarrow [D^{\delta+}A^{\delta-}]. \quad (1)$$

The theory of the CTC and their role in physical and chemical processes have already been considered[1-10], but virtually no systematic account has been given of data concerning the application of the electronic spectra of intermolecular CTC to the study of intramolecular interactions in donor and acceptor molecules, particularly in the case of organoelemental donors.

According to Eqn.(1), the appearance of fractional charges in D and A is accompanied by a redistribution of electron density in the molecules. However, for the ground state (GS) of weak π,π and π,σ complexes (which will be the subject of subsequent discussion) such redistribution is slight as a consequence of the small charge transfer from the donor to the acceptor[1,3]. In the ground states of the remaining complexes the contribution of the valence (donor–acceptor) interactions is not decisive in the overall balance of the intermolecular forces (see, for example, Foster[6]). When the complex undergoes a transition to an excited state, the electronic configurations of the species comprising the complex are altered even in the case of weak D–A bonds and the degree of charge transfer from D to A increases sharply. On the basis of the Mulliken theory[3], one can therefore speak of a new energetic state of the components of the complex—the charge-transfer state (CTS). In particular, the parameters of the electronic spectra of weak CTC contain information about this state. It is shown below that the intramolecular interactions in the ground and charge-transfer states as a rule do not differ in principle but many fine effects in the CTS are manifested more distinctly. Therefore the excited state of the CTC constitutes a convenient model for the investigation of a wide variety of problems associated with the distribution of electron density in the CTC components.

The main studies of recent years, devoted to the intramolecular interactions in the molecules of π-donors (derivatives of benzene, naphthalene, certain heterocyclic compounds, etc.) using the electronic spectroscopy of weak CTC, are analysed in this review. Particular attention is devoted to organoelemental π-donors.

II. ELECTRONIC ABSORPTION SPECTRA OF CHARGE-TRANSFER COMPLEXES

1. Principles of the Application of the Spectroscopy of Charge-Transfer Complexes in the Study of Intramolecular Interactions

The charge-transfer frequency ν_{CT} (the parameter which is most readily determined experimentally and is proportional to the energy of the transition with charge transfer) and the intensity of the charge-transfer band in the electronic absorption spectra of the CTC can be used to investigate the nature of the distribution of electron density in the donor molecules[3]. Fig.1 presents the energy diagram for a weak CTC, from which it follows directly that the energy of the electron transition with charge transfer is defined by the equality

$$h\nu_{CT} = W_E - W_N = W_E - \Delta H = I_D - E_A + E_C + R_E - W_N \quad (2)$$

where W_E and W_N are the energies of the excited and ground states of the CTC respectively, $W_N = \Delta H$ is the enthalpy of formation of the CTC (for weak complexes, $|\Delta H| < 10$ kcal mol^{-1}), I_D the "adiabatic" ionisation potential of the donor molecule, equal to the energy of the electronic transition from the lowest vibrational level of the ground state of the neutral molecule to the lowest vibrational level of the ion D^+, E_A the "adiabatic" electron affinity of the acceptor A, E_C the Coulombic energy whose evolution stabilises the complex in the excited state, and R_E the energy of the destabilisation of the excited complex due to the contribution of the structure D...A, the interaction in which is of the van der Waals type. The contribution of this structure to the ground state of the CTC is decisive[3], the system being stabilised by the "charge transfer energy" R_N.

The quantitative relation between the energy of the charge-transfer transition $h\nu_{CT}$, the ionisation potential of the donor I_D, and the electron affinity of the acceptor E_A is[1]

$$h\nu_{CT} = I_D - (E_A - E_C + W_0) + (\beta_0^2 + \beta_1^2)/[I_D - (E_A - E_C + W_0)], \quad (3)$$

where W_0 is the sum of the terms characterising the van der Waals interaction in the ground state, $\beta_0 = H_{01} - W_0 S$ and $\beta_1 = H_{01} - W_1 S$ are matrix elements with $H_{01} = \int \psi_0 H \psi_1 d\tau$ and $S = \int \psi_0 \psi_1 d\tau$, ψ_0 and ψ_1 being the wave functions of the structures D...O and D^+A^- respectively.

A parabolic relation between $h\nu_{CT}$ and I_D has been obtained for weak complexes of the π,π and π,σ types involving a series of isotypical donors and a constant acceptor[1]:

$$h\nu_{CT}=I_D-C_1+C_2/(I_D-C_1) \quad , \qquad (4)$$

where C_1 and C_2 are constants whose significance is clear from a comparison of Eqns.(3) and (4). For donors with ionisation potentials in the range $7 < I_D < 9$ eV, Eqn.(3) can be satisfactorily approximated by the linear relation[11]

$$h\nu_{CT}=aI_D+b \quad , \qquad (5)$$

where a and b are constants. For CTC between π-donors and iodine, $a = 0.87$ and $b = 0.36$.[1]

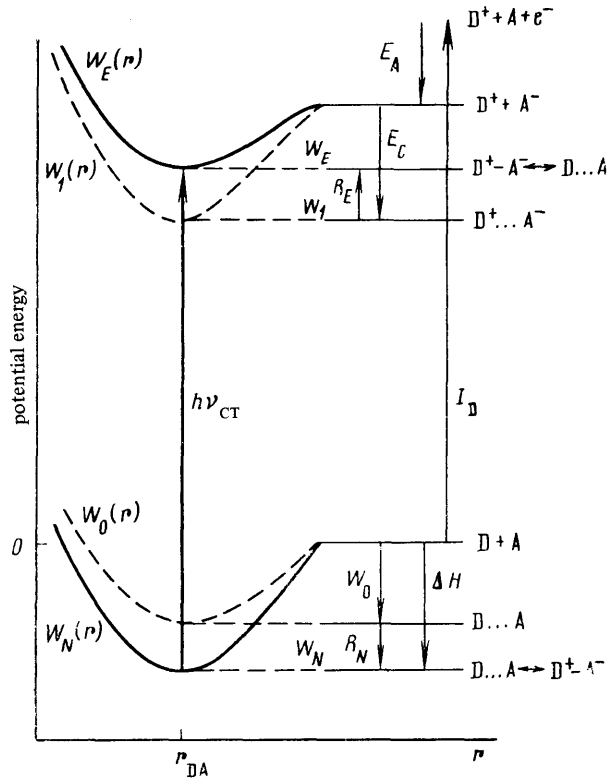


Figure 1. Energy diagram for a weak charge-transfer complex.

Eqn.(5) defines the dependence of the frequency ν_{CD} on the influence of the substituents and the donor, since I_D reflects the change in the donor–acceptor properties of the donor molecule on substitution. This follows, for example, from the Koopmans theorem[12], according to which the ionisation potential of the ith energy level of the molecule is approximately equal to the energy of the corresponding molecular orbital (MO) with the sign reversed.

On the other hand, the Hammett σ constants are traditionally used in physical organic chemistry for the estimation of the effects of substituents. The criterion of the applicability of a particular parameter (including the spectroscopic parameter) to the determination of the dependence of the reactivity of the structure is provided by a linear relation between the parameter and the σ constants[13,14]. It is also necessary that the correlated parameter should have the significance of the Gibbs free energy for the given process. The literature data (see, for examples, Ref.15–17), show the applicability of the Hammett relations to weak donor–acceptor interactions, i.e. the following linear relation holds for the ground states of π,π- and π,σ-complexes (as well as n,σ-complexes [5]):

$$\ln\frac{K_x}{K_0}=\rho_{CT}\sigma \quad , \qquad (6)$$

where K_x and K_0 are the equilibrium constants for the complex formation processes involving substituted (K_x) and (K_0) donors, ρ_{CT} is the reaction constant [corresponding to Eqn.(1)], which depends only on the type of process and characterises the sensitivity of the reaction centre to the influence of substituents, and σ is the constant of the substituent determined by its nature and position in the molecule.

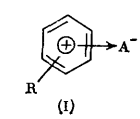
As for the usual chemical processes[13,14], the applicability of Eqn.(6) to the formation of CTC has been studied in detail for benzene derivatives. For three acceptors differing significantly as regards their electron affinities (the affinities[19] E_A are given in brackets), the values of ρ_{CT} (cal mol^{-1}) are as follows[18]: −0.41 for 1,3-dinitrobenzene (0.9), −0.59 for *p*-chloranil (2.0), and −0.98 for tetracyanoethylene (2,3). The low values of ρ_{CT} indicate a low degree of charge transfer in the ground states of weak CTC and a low sensitivity of the ground states of benzene derivatives (D) to the electronic influence of the substituents in processes of type (1). On transition of the CTC to an excited state, the degree of charge transfer increases sharply (for the excited state of the hexamethylbenzene–tetracyanoethylene complex, it is approximately 0.8 compared with 0.05–0.1 for the ground state[1]).

The values of ρ^*_{CT} (cal mol^{-1}) in the CTS of benzene derivatives (complexes with tetracyanoethylene) are between −10 (Kuznetsov et al.[20]) and −19 (Hanstein et al.[21]). This indicates, firstly, a high sensitivity of the charge-transfer state of the π-donors to the electronic effects of the substituents and, secondly, shows that the use of the excited states of the CTC as a model for the investigation of the mechanisms of certain electrophilic addition reactions is promising because the above values of ρ^*_{CT} are close to the values of ρ for many of the reactions characterised by an ionic transition state. It follows from the principle of the linear free energy relations[13] that[18,21]

$$(h\nu_{CT,x}-h\nu_{CT,0})/(2,3RT)=\rho^*_{CT}\sigma \quad , \qquad (7)$$

where $h\nu_{CT,x}$ and $h\nu_{CT,0}$ (cal) are the energies of the charge-transfer transitions of substituted and unsubstituted donor molecules respectively, R the gas constant, T(K) the absolute temperature, and ρ^*_{CT} (cal mol^{-1}) the reaction constant referring to the formation of an excited CTC. The energy of the charge-transfer transition and the σ constants of the substituents are in this case determined in a liquid solution, i.e. with allowance for the solvation effect.

The structure of the excited state of the CTC involving benzene derivatives is usually represented schematically as follows:



(I)

It is therefore possible to postulate that Eqn.(7) should hold best when the scale of the Brown–Okamoto electrophilic σ^+ constants[22], taking into account the positive charge on the reaction centre (the benzene ring is such a centre in relation to the π-acceptor), is used.

Eqns.(5) and (7) serve as a basis for the quantitative study of the influence of substituents on the reactivity of π-donors in a charge-transfer state. The appearance of a positive charge on the donor centre in the CTS does not significantly diminish the aromatic character of the π-donors. On the other hand, for ethylene derivatives (see below), where the positive charge is localised at the C = C bond, the multiplicity of the latter diminishes sharply in the CTC.[23]

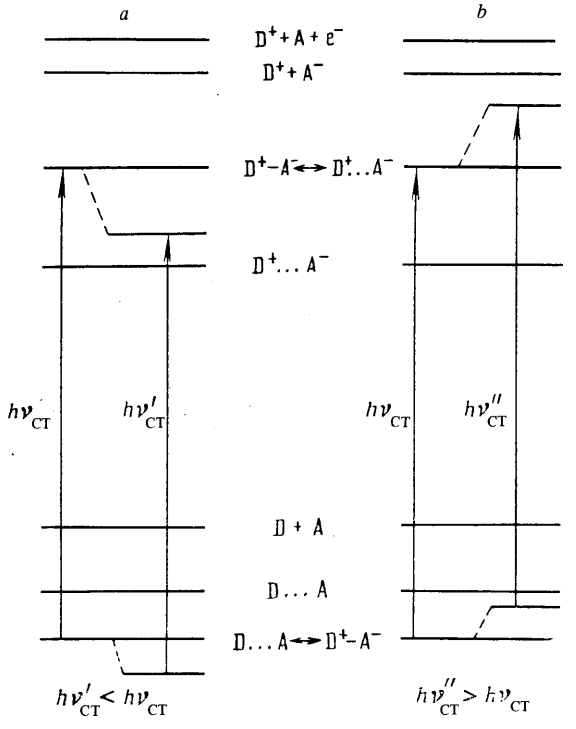


Figure 2. The influence of the electron-donating (*a*) and electron-accepting (*b*) substituents X on the positions of the energy levels in the ground and excited states of CTC for benzene derivatives of the type



a) *+I* or *+M* effect of the substituent; *b*) *–I* or *–M* effect of the substituent.

The influence of substituents on ν_{CT} (in the case of CTC derived from benzene) is illustrated clearly by the energy scheme for the CTC presented in Fig.2. The introduction of an electron-donating substituent increases the electron density in the ring via the inductive (*–I*) on conjugation (*–M*) mechanisms, which stabilises the ground and charge-transfer states of the complex. However, in view of the greater sensitivity of the CTS to electronic effects, already discussed above, the energy of this state diminishes to a greater extent after the introduction of a substituent of this kind. This results in a decrease of the energy of the charge-transfer transition ($h\nu'_{CT}$) of the donor molecule and in a bathochromic shift of the CT band in the electronic spectrum. The introduction of an electron-accepting substituent (with an *–I* or a *–M* effect) has the opposite effect, destabilising the complex and increasing the energies of the ground and charge-transfer states, the latter to a greater extent. This entails an increase of the energy of the charge-transfer transition ($h\nu_{CT}$), which is manifested by hypsochromic shifts of the CT band. The nature of the influence of the electronic nature of the substituent on the energy of the charge-transfer transition follows also from the molecular-orbital study of the formation of the CTC.[24]

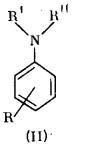
2. Benzene Derivatives

Charge-transfer complexes derived from benzene serve as model compounds for the investigation of many aspects of complex formation[25]. Comparison of the results of the study of the CTC by electronic spectroscopy with data obtained by independent methods makes it possible to obtain information about the mechanisms of the intramolecular interactions in various electronic states.

Such comparative analysis for a series of benzene derivatives has been carried out, for example, by Kuznetsov et al.[26]. The electron density at the donor centre in the CTS has been estimated in terms of the frequency ν_{CT} in the spectra of the complexes with tetracyanoethylene (TCE) and that in the ground state was estimated in terms of $\Delta\nu$, which is the frequency shift of the stretching vibration of the O–H bond of phenol in the infrared spectrum on formation of the O–H...π hydrogen bond between phenol and benzene derivatives. The $\Delta\nu$ and ν_{CT} for a series of compounds are linked by an empirical linear relation

$$\Delta\nu = -0{,}0074\ \nu_{CT} + 237 \qquad (8)$$

which shows that the effects of the substituents in the ground and charge-transfer states do not differ fundamentally. However, the experimental points for compounds with substituents having a lone electron pair (LEP)† [of the type of OCH_3, SCH_3, $N(CH_3)_2$, etc.] or substituents tending to become polarised in the CTS (I, $CH=CH_2$, etc.) deviate from Eqn.(8) towards lower values of ν_{CT}; the deviations δ (kcal mol^{-1}) = $\nu_{CT}^{exp} - \nu_{CT}^{calc}$ are between 10 and 20 kcal mol^{-1}. This is caused by the appearance of the electromeric *+E* effect in the CTS (increase of the n,σ, σ,π, and π,π conjugation as a consequence of the electron density deficit in the benzene ring) and by the significant contribution of the LEP of the heteroatom to the highest occupied molecular orbital (HOMO) in the corresponding compounds. We shall consider in greater detail the intramolecular interactions in the CTS of compounds of the type indicated.



(II)

$R' = R'' = H, CH_3$

†Here and henceforth in this review the $\Delta\nu$ and ν_{CT} are quoted in cm^{-1}.

The frequencies ν_{CT} in the spectra of the CTC of the aromatic amines (II) with TCE are linearly related to the basicity expressed by the pK:[27]

$$pK = -0.449 \cdot 10^{-3}\ \nu_{CT} + 11.05 \quad . \qquad (9)$$

o-Halogenoanilines do not obey this relation. Despite the π,π-character of the complexes of anilines with TCE, in the presence of halogens in the *ortho*-position there is a possibility of a direct overlap of the *p*-orbitals of the halogen atoms and the π-orbitals of the TCE molecule.

Tetracyanoethylene can react with aromatic amines[27] and it is therefore preferable to use weaker π-acceptors, for example, 1,3,5-trinitrobenzene (TNB).[28] The substituents examined by Kravtsov and Faingor[28] included a series of organomercury derivatives, so that information about the donor–acceptor properties of the Hg–X fragment was obtained from the ν_{CT} data. The following relation holds for the CTC of organic derivatives of dimethylaniline and TNB:

$$\nu_{CT} = 2130\sigma_p^+ + 20490;\ \dot{\rho}_{CT} = -4.49^{\dagger} \quad . \qquad (10)$$

It was used to calculate the σ_p^* constants of the substituents[28]. When organomercury substituents are introduced into the ring, the CT band undergoes a hypsochromic shift, which indicates the electron-accepting properties of such substituents. For α-substituted *N*,*N*′-dimethyl-*p*-toluidines, there is a linear relation between ν_{CT} and the inductive σ_I constants of the substituents in the methyl group:

$$\nu_{CT} = 3120\sigma_I + 19550;\ \dot{\rho}_{CT} = -6.58\ (r = 0.971) \quad . \qquad (11)$$

This indicates a predominantly inductive interaction of the substituent with the aromatic ring. An analogous correlation has been obtained for organomercury substituents of the type of HgX with different X:

$$\nu_{CT} = 2880\sigma_I + 19960;\ \dot{\rho}_{CT} = -6.07\ (r = 0.991) \quad . \qquad (12)$$

It follows from Eqns.(11) and (12) that the transmission properties of the mercury atom are weaker than those of the methylene unit.

The spectra of the CTC formed by compounds of the type $C_6H_5ECH_3$ (E = O, S, Se, or Te) (III) have been investigated in fair detail. The electron-donating properties of compounds (III) increase on passing from E = O to E = Te,[29] apparently mainly as a result of the increasing *n*-character of the highest occupied molecular orbital. Indeed the ionisation potentials of the *n* electrons of sulphur, selenium, and tellurium are smaller than the first ionisation potential of benzene and the orbital of the heteroatom therefore makes the main contribution to the HOMO of thio- and seleno-anisoles. The nature of the HOMO of the anisole molecule is determined by the symmetrical π_S-orbital of the ring, because the ionisation potential of the *n* electrons of the oxygen atom is greater than the first ionisation potential of benzene. Nevertheless all compounds of type (III) are donors of the π-type.

The electron-donating properties of the compounds XC_6H_4-ECH_3 (IV) become weaker as the position of X varies in the series *para*- > *ortho*- > *meta*-.[29] Owing to steric interactions, in *ortho*-substituted compounds (IV) there is a possibility of a breakdown of the coplanarity of X and the remainder of the molecule, which leads to an alteration of the electron-donating capacity of the compound as a whole[29,30]. As was to be expected, the electrophilic σ^+ constants proved to be preferable to the usual Hammett σ constants for the description of the correlation with ν_{CT} in the spectra of the CTC formed by compounds (IV).[31,32] The sensitivity of the HOMO to substitution in the ring of compound (IV) diminishes in the series of substituents O > S > Se as a consequence of the increasing localisation of the HOMO at the heteroatom and the appreciable conformational inhomogeneity (see also Vtyurina and Chmutova[34]).

The substituents have a complex influence on the ν_{CT} in the spectra of CTC formed by compounds of the type C_6H_5ER (V).[33] For E = O, the frequencies ν_{CT} vary in the following sequence of R: $CH_3 > C_2H_5 >$ iso-$C_3H_7 \ll$ t-C_4H_9. The sequence R = $CH_3 \cong C_2H_5 <$ iso-$C_3H_7 \ll$ t-C_4H_9 holds for sulphides and selenides. The conformation of the molecules of compounds (V) depends on the nature of E. Planar conformers are obtained for E = O, in which R influences the conjugated system mainly inductively and a non-planar configuration and the steric inhibition caused by this is possible only for R = t-C_4H_9. For E = S or Se, the steric effects of the substituents R are stronger and there is monotonic decrease of the energy of the HOMO with increasing bulk of R.

Variation of the bulk of the group R alters the ratio of the intensities of the long-wavelength and short-wavelength bands in the electron absorption spectra of CTC of compounds (V),[34] as in other benzene derivatives[36,37]. Bulky substituents (of the type of t-C_4H_9) decrease the intensity of the long-wavelength band both as a result of the decrease of the electron-donating capacity of the substituents as a consequence of the decrease of n,π conjugation and as a result of the increase of the contribution of the "transverse" orientation of the complex for steric reasons[35].

In contrast to the isologous anisoles, the intramolecular interactions in the CTS of phenol derivatives have been less thoroughly studied. The following linear correlations between ν_{CT} and σ^+ constants have been established for phenol derivatives:

(a) Monosubstituted phenols[38]:

$$\nu_{CT} = 5000\sigma_p^+ + 20500;\ \dot{\rho}_{CT}^+ = -10.0\ (r = 0.998)\ ; \qquad (13)$$

(b) *para*-Substituted 2,6-di-t-butylphenols[39]:

$$\nu_{CT} = 2830\sigma_p^+ + 17400;\ \dot{\rho}_{CT}^+ = -5.9\ (r = 0.992) \quad . \qquad (14)$$

A linear relation between ν_{CT} and $\Delta\nu$ (a property of the ground state) holds for monosubstituted phenols[38]. In contrast to benzene derivatives (see above), $\Delta\nu$ represents in this instance the shift of the stretching vibration frequency of the O–H bond in the infrared spectra of phenols on formation of an intermolecular hydrogen bond by the latter with tetrahydrofuran (a characteristic of the acidity of phenols). The points corresponding to compounds containing the O or S heteroatom deviate from the relation

$$\Delta\nu = 0.0194\ \nu_{CT} - 90\ (r = 0.970) \qquad (15)$$

towards lower values of ν_{CT}. The cause of the deviation is the same as for the benzene derivatives examined above—enhancement of the degree of n,π conjugation of the electron-donating substituents on passing from the ground state (*+M* effect) to the CTS (*+E* effect) and the increase of the *n*-character of the HOMO. The presence of even one bulky substituent in the *ortho*-position relative to the OH group alters the nature of the intramolecular interactions in phenol derivatives[40].

The quality of the $\nu_{CT} = f(\sigma^+)$ correlations improve somewhat when σ^+ and σ^- constants are used simultaneously: for more than 30 trisubstituted phenols with two *ortho*-substituents, the following relation holds according to the

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#Here and henceforth $\dot{\rho}_{CT}^*$ (cal mol^{-1}) is the slope of the plot of $\nu_{CT} = f(\sigma)$ [see Eqn.(7)].

data of Sennikov et al.[39]:

$$\nu_{CT}=3840\Sigma(\sigma^{+}+\sigma_{o})+18900 \quad . \qquad (16)$$

The considerable role of steric effects in the CTS is also indicated by the absence of a simple relation of type (15) for *ortho*-substituted phenols[40]. The significant decrease of the absolute value of the constant ρ^{*}_{CT} for shielded phenols [cf. Eqns.(13) and (14)] implies a decrease of the sensitivity of the HOMO of 2,6-di-t-butylphenols to structural changes in the molecule in the CTS, caused evidently mainly by the steric effects of the two t-butyl groups. The absence of fundamental changes in the influence of the *para*-substituent on transition of the molecules of 2,6-di-t-butyl phenols from the ground states to the CTS is indicated by the linear relation between ν_{CT} and the integral intensity $A^{1/2}$ of the ν(O–H) band in the infrared spectra of phenols[39]:

$$A^{1/2}\ (\text{mol}^{-1/2}\ \text{litre}^{1/2}\ \text{cm}^{-1}) = 0.69\cdot10^{-4}\nu_{CT}+0.056\ (r=0.980). \qquad (17)$$

A property of phenol derivatives which is of practical importance, namely their antioxidant capacity, characterised quantitatively by the rate constant k for the chain termination reaction in the radical oxidations of hydrocarbons [reaction (18)] or some other quantities[43], is linearly related to the energy of the HOMO of phenols[41,42]:

$$R'OO^{\cdot}+ROH\xrightarrow{k}R'OOH+RO^{\cdot} \quad . \qquad (18)$$

This enabled Lloyd[44] and Razuvaev et al.[45] to compare the ν_{CT} in the spectra of the CTC between phenols and TCE with data for the antioxidant activity. There is a parallel variation of ν_{CT} and the residual strain in the polymers, characterising the degree of their degradation[44]. A quantitative relation has also been established[45] between the logarithms of the rate constant of reaction (18) (R′ = styrene) and ν_{CT} in the spectra of the CTC formed by *meta*- and *para*-substituted unshielded phenols and *para*-substituted 2,6-di-t-butylphenols:

$$\ln k\cdot10^{-3}=-7.67\cdot10^{-4}\ \nu_{CT}+16.70\ (r=0.999)\ ; \qquad (19)$$

$$\ln k\cdot10^{-3}=-10.13\cdot10^{-4}\ \nu_{CT}+18.80\ (r=0.996)\ . \qquad (20)$$

These results make it possible to regard ν_{CT} as a characteristic of the inhibiting capacity of phenolic antioxidants.

The study of the intermolecular interactions in the CTS of the ether XC_6H_4-OR (R is a constant fragment capable of conjugation with the heteroatom), can yield information about the involvement of the heteroatom (oxygen) in the transmission of conjugation effects. The nature of the conjugation effects in molecules of *para*-substituted phenyl vinyl and isobutenyl phenyl ethers XC_6H_4-O-CH = $C(CH_3)_2$ (VI) has been considered by quantum-mechanical methods, by the spectroscopy of the CTC with TCE, and by kinetic procedures[46,47]. A linear relation between the energy of the HOMO and the σ^{+}_{p} constants of the constituents in the benzene ring follows from the calculations of the electronic structure in the ground state of phenyl vinyl ethers[47]:

$$E_{HOMO}=0.58\sigma^{+}_{p}+10.92. \qquad (21)$$

This molecular orbital is localised mainly on the oxygen atom and on the alkene carbon atoms. There is a linear correlation between $h\nu_{CT}$ and the σ^{+}_{p} constants for compounds (VI)¶:

$$h\nu_{CT}=0.56\sigma^{+}_{p}+2.39;\ \rho^{+}_{CT}=-9.4\ (r=0.990)\ . \qquad (22)$$

¶Here and henceforth the values of $h\nu_{CT}$ are expressed in eV.

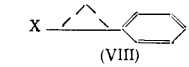
According to Donnay et al.[46], the similar slopes of relations (21) and (22) confirm the presence of a common conjugational system in molecules of isobutenyl phenyl ether (VI) [we may note that the correlation expressed by Eqn.(22) apparently refers to the CTS and not to the ground state of the molecule of compound (VI) as suggested by Donnay et al.[46]]. Quantum-mechanical calculations on analogous molecules[29] also indicate the presence of a single conjugated aromatic ring–heteroatom–double bond system in which the nature of the HOMO is determined by the interaction of the heteroatom not only with the ring but also with the α,β-double bond (in contrast to, for example, allyl derivatives where the influence of the double bond in the β,γ-position relative to the heteroatom is of subsidiary importance). However, the contribution of the heteroatom to the HOMO (i.e. its involvement in the transmission of conjugation effects) becomes significant only for C = S or Se. As already mentioned, for ethers the contribution of symmetrical π_S-orbitals of the ring predominates. This was confirmed by the impairment of the correlation between ν_{CT} and the σ^{+} constants on passing from ethers to selenides. The role of the conformational effect increases in the same sequence[31]. The high accuracy of correlation (22) therefore indicates that the coordination of the TCE molecule to the benzene ring predominates.

The intramolecular interactions in the CTS of aryl benzyl ethers $C_6H_5CH_2OC_6H_4X$ (VII) have been investigated[48]. In this case the correlation between $h\nu_{CT}$ and σ^{+} is

$$h\nu_{CT}=0.45\sigma^{+}_{p}+2.40;\ \rho^{+}_{CT}=-7.66\ (r=0.970) \quad . \qquad (23)$$

Unfortunately we are unaware of studies devoted to complexes of derivatives of diphenyl ether with TCE. Comparison of such data with the above results[48] would enable one to elucidate the role of the methylene unit in the transmission of electronic effects in the CTS.

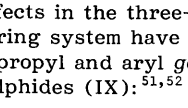
Brown and Treylor[49] examined the intramolecular interactions in the CTS of 2-substituted phenylcyclopropanes (VIII):



(VIII)

It follows from the electronic spectroscopic data for the CTC of these compounds with TCE that the cyclopropyl group is a much more powerful electron donor than, for example, the ethyl group. The authors[49] attribute this to the σ,π conjugation of the cyclopropane and benzene fragments. However, the substituents X in the 2-position in the three-membered ring (for example, the methoxy-group) hardly influence the donor–acceptor properties of the molecule of compound (VIII) in the CTS. From this, one can conclude that the ability of the cyclopropyl group to transmit the π-electronic effect in the CTS is negligible, which is confirmed by the results of Mancini et al.[50]

The conjugation effects in the three-membered ring–heteroatom–benzene ring system have been considered in relation to aryl cyclopropyl and aryl *gem*-dichlorocyclopropyl ethers and sulphides (IX):[51,52]



(IX)

$R^{I}=R^{II}=H, Cl;\ E=O, S$.

The ν_{CT} data for the complexes of compound (IX) with TCE (classified as of the π,π-type) indicate the electron-accepting properties of the cyclopropane fragment of the molecule of

compound (IX) in the CTS, which is determined by both the inductive ($-I$) and conjugation effects.

The intramolecular interactions in phenyl derivatives of group (VIa) elements of different complexity have been investigated in a series of studies[53-56,59] (data for the ν_{CT} and the equilibrium constants K_C for complexes with π- and σ-acceptors were used). It was shown that the electron-donating properties of the diaryl ethers, sulphides, and selenides as well as the stability of their complexes with iodine (CTC of the n,σ-type) become enhanced in the sequence O (K_C = 0.39 litre mol^{-1}; ν_{CT} = 29000 cm^{-1}) < S (3.90; 28600) < Se (27.8; 28200).[54] The increased stability of the selenium complexes compared with the sulphur-containing analogues is due to the high basicity and large size of the selenium atom[53,54]. The equilibrium constants for the CTC of substituted diphenyl sulphides increase with decrease of ν_{CT}, i.e. as the electron-donating properties of the sulphides become more pronounced[54]. The quantity ρ_{CT} for the correlation between $\lg K_C$ and σ for diphenyl sulphides (−0.54) is somewhat smaller than the corresponding values for thiophenols (−1.11).[53] This is associated with the smaller change in electron density at the sulphur atom under the influence of substituents as a consequence of the conjugation intramolecular transmission of the electronic effects between the two phenyl groups via the bridging sulphur atom. Another cause of the decreased sensitivity of diphenyl sulphides to structural changes is apparently associated with the steric hindrance by the phenyl groups of the approach of the σ-acceptor to the reaction centre (the sulphur atom).

The ability of the selenium bridge to transmit the electronic effects between two aromatic systems is much smaller than that of the sulphur-containing bridge, which can be seen from the high value $\rho = -2.1$ for diphenyl selenides, indicating a high sensitivity of the electron density at the selenium atom to external perturbations. The introduction of a methylene fragment between the heteroatom and the benzene ring (the CTC of aryl benzyl sulphides with iodine[54,57]) disturbs the transmission of electronic effects described above. The study of the spectra of the CTC of diphenyl sulphides with TCE showed[55,56] that *para*-substituted sulphides exhibit the most marked electron-donating properties as a consequence of the direct polar conjugation of the LEP of the heteroatom with *para*-substituents (Cl, OCH_3, etc.) via the π-electron system, mentioned above for thio- and seleno-anisoles. The anomalously weak electron-donating properties of bis(*o*-dimethylphenyl) sulphide (compared with those of alkyl sulphides) have been considered[55] as a result of the breakdown of the conjugation of the LEP of the sulphur atom with the two benzene rings. The marked conformational changes in such compounds have been confirmed by data obtained by independent methods[58]. The correlation between $\lg K_C$ and the σ constants of TCE is characterised by $\rho = -0.74$, which is close to $\rho = -0.64$ obtained for the CTC of the same sulphides with iodine[54]. This result suggests that the HOMO in these and other complexes are isotypical.

It is known[1] that the K_C for the complexes of typical π-donors with TCE are higher than for CTC with I_2. As the n-donor character is enhanced, the K_C of the complexes with iodine increase and for the pure n-donors they are much higher than the K_C for the complexes with TCE. The K_C for the complexes of diphenyl sulphides[55] with iodine are somewhat higher than those for the complexes with TCE, which indicates a mixed n,π-character of the HOMO of diphenyl sulphides.

This problem has been considered in more detail in relation to aryl diphenylmethyl sulphides $X^1C_6H_4(X^2C_6H_4)CHSC_6H_4Y$ (X).[56,59] The two phenyl fragments and the thiophenyl system are in this instance potential donor centres. Analysis of the ν_{CT} and the K_C for the complexes of compounds (X) with TCE and iodine shows that electrophilic attack by the iodine atom is directed preferentially to the sulphur atom (HOMO of the n,π-type) and not to the diphenylmethyl system. The effect of the substituent X is determined by the inductive mechanism and the sensitivity of the complex formation reaction with I_2 to the influence of the substituent is low because of the long distance between the substituent and the sulphur atom. The fragment Y acts on the sulphur atom via both inductive and resonance mechanisms and the resulting effect is approximately four times greater. The interaction of compounds (X) with a π-acceptor (TCE) is of an appreciably more complex type: TCE interacts with both the phenylthio-system and with the diphenylmethyl group.

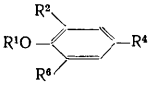
The intramolecular interactions in large series of disulphides and diselenides of the type $X-C_6H_4-E-E-C_6H_4-X$ (XI, E = S or Se) have been investigated[60]. Whereas the CTC of aromatic disulphides with I_2 have not been detected spectrophotometrically[53], the complexes of diaryl diselenides absorb in the range 270–390 nm. The linear relation between ν_{CT} and σ^+ is characterised by the quantity ρ^*_{CT} = −2.0. According to the authors[60], in the case of compounds (XI) a single molecular orbital, incorporating not only the central fragment $-C_6H_4-Se-Se-C_6H_4-$ of the test molecules but also the substituents X, is involved in the formation of complexes. As in the monosulphides and monoselenides, in aromatic disulphides and diselenides the intramolecular interactions are strongly manifested between substituents in the *para*-positions in the benzene rings. The sharp difference between the electron-donating properties of diaryl disulphides and diaryl diselenides in relation to iodine can be explained by the fact that the LEP of the sulphur atoms in the $(XC_6H_4)_2S_2$ molecules are incorporated to a greater extent in the π-system of the conjugated multiple bonds compared with the $(XC_6H_4)_2Se_2$ molecules. Comparison of the reaction constants for the CTC of compounds (XI) with TCE (ρ^*_{CT} = −2.89 for the sulphides and −2.04 for the selenides) indicates a somewhat greater sensitivity of the sulphur-containing compounds to the electronic effects of substituents (an analogous relation has been observed also for thio- and seleno-anisoles). The sensitivity of the disulphides greatly increases (ρ^*_{CT} = −7.32) when one of the phenyl groups in compounds (XI) is replaced by a methyl group.

We shall now consider the intramolecular interactions in the CTC of aryl derivatives of Groups IVB elements. In view of the lower electronegativity of the silicon atom (1.9) compared with that of carbon (2.6) [61] and the high inductive constant of the trimethylsilyl group [$\sigma^* = -0.9$ compared with $\sigma^* = -0.3$ for $C(CH_3)_3$],[63] an enhancement of the electron-donating properties of organosilicon derivatives compared with their carbon analogues may be expected. However, the results of spectrophotometric studies on the CTC of the compounds C_6H_5-X (XII) indicate the opposite situation[62]. This finding can be accounted for by the manifestation of the effect of the $d_\pi-p_\pi$ interaction due to the partial transfer of the π-electron density from the benzene ring to the vacant 3*d* orbitals of silicon, which acts in opposition to the $+I$ effects of the silyl groups.

Different aspects of this effect have already been considered[64]. The group $CH_2Si(CH_3)_3$ has more marked electron-donating properties than the trimethylsilyl group. Thus the following series based on the variation of the electron-donating properties of compounds (XII) as a function of X has been established: $CH_2Si(CH)_3 > CH_3 >$

$Si(CH_3)_3$; it is valid also for compounds containing several substituents in the ring[62].

Different aspects of the effects of the d_π–p_π interaction and σ,π conjugation in the charge transfer state have been considered[65–67].



(XIII)

Analysis of the values of ν_{CT} in the sterically hindered organosilicon phenols and ethers (XIII) shows[68] that the replacement of the $(CH_3)_3C$ group by $Si(CH_3)_3$ leads to an increase of ν_{CT} and hence to an enhancement of the electron-accepting properties of the phenols (in relation to the larger series of organosilicon and organogermanium phenols, this problem has been considered by Sennikov et al.[39]). An analogous relation has been observed also for the organosilicon ethers [$R^1 = Si(CH_3)_3$]; comparison of the values of ν_{CT} for the latter with the ν_{CT} for phenols shows that the trimethylsilyl group of the $Ar–O–Si(CH_3)_3$ fragment is a stronger electron acceptor than $C(CH_3)_3$ or the hydrogen atom.

Consequently the effect of the d_π–p_π interaction does not remain unchanged and depends significantly on the nature of the substituent X in the $(CH_3)_3Si$-X fragment. This observation has been confirmed by the study of the CTC of *para*-substituted organosilicon ethers p-XC_6H_4–O–Y (XIV) (compared with anisoles).[69,70] Whereas compounds (XIV) with $Y = Si(CH_3)_3$ exhibit weaker electron-donating properties compared with anisoles, with $Y = CH_2Si(C_2H_5)_3$ there is a considerable enhancement of the π-donor properties. The separation of the oxygen and silicon atoms by the $-CH_2-$ group disturbs the d_π–p_π interaction of the LEP of the oxygen atom with the 3*d* orbitals of silicon[71], which is manifested by a lower sensitivity of the HOMO of the molecule of compound (XIV) with $Y = CH_2Si(C_2H_5)_3$ to the electronic effects of substituents compared with compounds (XIV) in which $Y = Si(CH_3)_3$.

Analysis of the donor–acceptor properties of organosilicon ethers with the groups O–Si≤, O–Si–Si≤, and O–CH_2–Si≤ [71] leads to the conclusion that the *n*-orbital of the oxygen atom interacts with the π_s-orbital of the benzene ring. The influence of the organic substituent R in C_6H_5OR on the nature of the HOMO is weak and is transmitted mainly via the inductive mechanism. It is believed essential[71] to take into account the interaction of the LEP of the oxygen atom with the σ orbitals of the neighbouring C–Si or Si–Si bonds in the ethers with $R = Si(CH_3)_3$, $CH_2Si(CH_3)_3$, or $Si_2(CH_3)_5$ (taking into account photoelectron spectroscopic data).

The electronic absorption spectra of the CTC of more than 70 organosilicon and organogermanium derivatives of benzene with TCE have been considered in a number of studies[65–67], where the electronic effects of the organoelemental substituents in the ground and charge-transfer states were also compared. The donor–acceptor properties of the compounds in the ground states were characterised in terms of the quantity $\Delta\nu$ (see above). The points corresponding to compounds with substituents whose degree of conjugation with the ring does not change significantly on transition from the ground to the charge transfer state fit on the plot of Eqn.(8) described above. Such substituents include also fragments with the M–Ar bond (M = Si or Ge), which indicates the constancy of the manifestation of the d_π–p_π interaction in the ground and charge transfer states. The points corresponding to the benzyl derivatives of silicon and germanium deviate from correlation (8) towards lower values of ν_{CT} (analogously to the derivatives of benzene with substituents containing a heteroatom with LEP). The anomalously pronounced electron-donating properties of benzyl derivatives can be explained by the effect of the σ,π conjugation of the C–M bond with the benzene ring in the CTS.[65] For the benzyl derivatives of silicon and germanium, the σ,π conjugation occurs even in the ground state but, on passing to the CTS, it becomes much more marked[67]. The effect of the σ,π conjugation is impaired after the introduction of a second methylene group into the molecule (compounds of the type $C_6H_5CH_2CH_2MR_3$).[72] The degree of σ,π conjugation diminishes following the enhancement of the electron-accepting properties of the substituents at the atom M.[73]

Specific electronic effects obtain for organosilicon derivatives of benzene with an Si–Si bond. Recently the interaction of the Si–Si σ-bond with unsaturated fragments has been studied by various physical methods, including spectrophotometry of the CTC.[62,74–78] Analysis of the CT band in the electronic spectra of complexes of benzene derivatives containing the SiR_2SiR_3 and CH_2SiR_3 groups has shown[62] that the ν_{CT} of the long-wavelength bands corresponding to these compounds are 20200 and 20400 cm^{-1} respectively. Thus the disilanyl substituent exhibits the same σ-donor properties as the trimethylsilylmethyl substituent, the properties being more marked than the electron-accepting properties of the same fragment due to the d_π–p_π interaction. Subsequent studies[74–78] confirmed the occurrence of σ(Si–Si)–π conjugation in phenylpolysilanes. The electron-accepting properties of fragments containing the polysilicon chain are apparently determined by the silicon atom which is closest to the benzene ring[78].

The determination of the coordination centre of the π-acceptor (TCE) in the study of the intramolecular interactions in the π-complexes of metals (data for the CTC of cyclopentadienyl derivatives of iron, cobalt, and nickel[4,79]) has been the subject of controversy; the problem was whether this centre is the cyclopentadienyl ring or the metal atom[80,81]. The authors of two reviews[4,79] believe that the compounds most probably form complexes of the π,π-type. This question has been investigated for arenechromium, arenemolybdenum, and arenetungsten tricarbonyls of the type $XC_6H_5M(CO)_3$ (XV, M = Cr, Mo, or W).[82–86] It has been concluded[83,84] that there are two coordination centres in arenemetal tricarbonyls—the benzene ring in complexes with TNB and the metal atom in complexes with TCE. However in other studies[85,86] data for the CTC spectra have been interpreted from the standpoint of the coordination of both π-acceptors solely to the aromatic ring.

The following relations have been obtained for the complex-formation reactions of arenechromium tricarbonyls with TNB (a weak π-acceptor) and TCE (a strong π-acceptor):[86]

$$\text{TNB}: \nu_{CT} = 1060\Sigma\sigma^+ + 20700;\ \rho^*_{CT} = -2.23\ (r = 0.870)\ ; \quad (24)$$

$$\text{TCE}: \nu_{CT} = -1550\,\Sigma\sigma^+ + 13300;\ \rho^*_{CT} = +3.27\ (r = 0.950)\,. \quad (25)$$

The inversion of the sign of the reaction constant ρ^*_{CT} on passing from complexes with TNB to those with TCE indicates a change in the mechanism of the transmission of electronic effects. This change is associated with the ability of the $Cr(CO)_3$ group to manifest electron-accepting properties in the presence of a fairly small positive charge on the ring (complexes with TNB, $\rho^*_{CT} < 0$) and electron-donating properties when there is an appreciable deficit of electron density at the donor centre (complexes with TCE, $\rho^*_{CT} > 0$). For CTC with *p*-chloranil, *p*-bromanil. and trinitrophenol, which have intermediate E_A values, the correlation between ν_{CT} and σ^* constants is impaired, which indicates a smooth

variation of the mechanism of the transmission of the electronic effects in the system $Cr(CO)_3$ group–benzene ring–π-acceptor. The following series based on the enhancement of the electron-accepting properties of arenemetal tricarbonyls has been obtained from spectrophotometric data for the CTC of compounds (XV) with TCE:[86] Cr < Mo << W.

Relations of the type $\nu_{CT} = f(\sigma)$ make it possible to apply the spectrophotometry of the CTC to the evaluation of the σ constants of the substituents. It was shown in the introduction to this review that the greatest efficiency of this method is to be expected in the calculation of the σ^+ constants. On the other hand, the possibility of using this method also for the determination of σ constants using the equation

$$\nu_{CT} = 10\,000\,\Sigma\sigma + 23\,900 \quad . \qquad (26)$$

has likewise been demonstrated[87,88].

Eqn.(26) holds only for benzene derivatives without substituents whose electronic influence increases sharply on transition from the ground to the charge-transfer state. Otherwise one must employ either the equation[21]

$$\nu_{CT} = 9200\sigma_p^+ + 26200 \quad , \qquad (27)$$

or, according to Kuznetsov et al.[65], the equation

$$\nu_{CT} = 5260\sigma_p^+ + 24800 \quad . \qquad (28)$$

The significant difference between the slopes of relations (27) and (28) can be explained by the different methods used to derive them. Eqn.(27) has been derived for several benzene derivatives containing substituents with known σ^+ constants in the range 0 to −1.4, while Eqn.(28) has been obtained by combining two equations[87,88]:

$$I_D\ (eV) = 0.80\sigma_p^+ + 9.67 \quad ; \qquad (29)$$

$$\nu_{CT} = 7500\ I_D - 41\,000, \quad . \qquad (30)$$

Eqn.(29) is valid only for mono- and di-substituted benzenes. When the equation for a large series of polysubstituted benzenes[89] is used instead of Eqn.(29), the numerical values of the parameters in Eqn.(28) approach those in Eqn.(27). Despite these deficiencies, Eqns.(27) and (28) are used to calculate the σ_p^+ constants for different substituents, including organoelemental substituents[21,65,90].

An attempt has been made to calculate the inductive σ_I constants of substituents of the type CH_2CR_3 from spectrophotometric data for CTC.[91]

3. Naphthalene Derivatives

There are a number of reviews on the CTC of naphthalene derivatives[1,2,4], but the available data on the intramolecular interactions in the CTC of these compounds are fragmentary. In contrast to the benzene derivatives[92,93], the electronic absorption spectra of the CTC of substituted naphthalenes exhibit three bands (which is consistent with the molecular orbital theory[62]), the third shortest-wavelength band having a very low intensity. The influence of the substituents on the first and second CTC bands is analogous to that of benzene but the sensitivity to this influence of the charge-transfer transitions corresponding to these bands depends on the type of substitution (see, for example, Evans et al.[94]). The introduction of both the $C(CH_3)_3$ and $Si(CH_3)_3$ groups increases the energy of the HOMO of naphthalenes (compared with the unsubstituted derivatives) as a consequence of the inductive +*I* effect (the bathochromic shift of both bands in the spectrum corresponds to this)[94]. However, despite the large +*I* effect of the trimethylsilyl group for organosilicon derivatives, a large bathochromic shift of the CT bands is not observed owing to the effect of d_π–p_π interaction in silylnaphthalenes.

Analysis of the ν_{CT} data also shows that, for 1-, 1,4-, and 1,5-substituted derivatives, the first (long-wavelength) band is more sensitive to the electronic influence, whereas for 2-, 2,6-, and 2,7-derivatives the second (short-wavelength band) is more sensitive. The effect of the d_π–p_π interaction in naphthalene derivatives has also been studied by Kuznetsov et al.[95]; it was found that 1-substituted derivatives have more pronounced electron-donating properties than 2-substituted derivatives, which agrees with the data of Evans et al.[94] The NH_2, OCH_3, and OH groups are significantly stronger electron donors in relation to the hydrogen atom than the $Si(CH_3)_3$ group, which again indicates the d_π–p_π interaction between the 3*d* orbitals of the silicon atom and the naphthalene ring.

The study of the intramolecular interactions in the CTC of 1-substituted naphthylpolysilanes[78] established the following series based on the enhancement of the electron-donating properties of the substituents: H < $Si(CH_3)_3$ < CH_3 < $Si_2(CH_3)_5$ < n-$Si_3(CH_3)_7$ < iso-$Si_3(CH_3)_7$ < $Si(CH_3)_3CH_2$. In contrast to benzene polysilicon compounds, the ionisation potential of the naphthalene system (8.12 eV) is lower than that of the σ-system of the substituents, including polysilanes: 8.69 eV for $Si_2(CH_3)_6$ and 8.19 eV for $Si(CH_3)_3$.[78] Therefore, when the molecular σ- and π-orbitals in naphthylpolysilanes overlap, the HOMO is mainly of the π-character. The data for the CTC spectra of 1- and 2-substituted naphthylpolysilanes have been discussed[96] from the standpoint of the σ,π conjugation of the Si–Si bond with the π-system of the naphthalene ring, but the authors unjustifiably neglected the d_π–p_π interaction.

4. Derivatives of Ethylene and Cyclopropane and Saturated Compounds

The study of the spectra of the CTC of alkyl vinyl ethers CH_2 = CH–OR (XVI) with TCE established[97] that the electron-donating properties of compounds (XVI) in the CTC increase in the following sequence of R: CH_3 < C_2H_5 < iso-C_3H_7 < t-C_4H_9, which agrees with the reactivity data[97]. We may note that a somewhat different relation has been observed for compounds (V), which are formal analogues of compounds (XVI). The view[97] that in alkyl vinyl ethers (in contrast to the aromatic analogues) the effects of the conjugation of the alkoxy-group with the double bond play a secondary role must be regarded as insufficiently well founded from the standpoint of the results of the study of Lopatin et al.[98].

Comparison of the frequencies ν_{CT} in the spectra of the CTC of the alkenyl derivatives of silicon of the type CH_2 = CH–$(CH_2)_n$–SiR_3 (XVII) (*n* = 1, 2) and the related carbon compounds with TCE on the basis of the results of Kuznetsov et al.[99] does not rule out the possibility of an interaction of the d_π–p_π type between the Si–C and C = C bonds for *n* = 1 in the CTS. In reality the usual σ,π conjugation is evidently an interaction of this type. A comparative study of the intramolecular effects in the alkenyl derivatives of carbon, silicon, germanium, and tin in the ground and charge-transfer states has been carried out[98]. The electronic influence of the substituents in the ground state was characterised, as for benzenes[26], by the frequency shift Δν of the stretching vibration of the O–H bond in the infrared spectrum of phenol (an electron acceptor) when it forms hydrogen bonds with the π-systems of ethylene derivatives. The electronic effects in the CTS are characterised by the value of ν_{CT} in the spectra of the CTC with iodine.

The data of Lopatin et al.[98] indicated an important role of the effects of the d_π–p_π interaction and σ,π conjugation in the ground and charge-transfer states. The electronic effects in the ground and charge-transfer states of a number of compounds are linearly related:

$$\Delta\nu = -0.00806\ \nu_{CT} + 342\ (r = 0.980). \qquad (31)$$

In contrast to the benzyl derivatives of silicon and germanium, the experimental points for the alkyl derivatives are consistent with Eqn.(31), which indicates the absence of a sharp increase of the effect of the σ,π conjugation in the allyl derivatives of the elements of the silicon subgroup on transition from the ground to the charge-transfer state.
A number of features, which have not been noted for benzene derivatives, have been observed for ethylene derivatives[26], which is associated[98] with the lower multiplicity of the carbon–carbon bond compared with the π-system of the benzene ring in the CTS. The substituent $(CH_3)_3SiSi.(CH_3)_2$ participates in two opposite effects of conjugation with the multiple bond: the d_π–p_π effect (electron accepting) and the σ,π effect (electron donating)[98]. According to some data[77,78], the influence of the second effect predominates.

Cyclopropane and its organic and organosilicon derivatives also form CTC with iodine[1,99]. As the electron-accepting properties of the substituent at the silicon atom linked to the cyclopropane ring are enhanced, a hypsochromic shift of the CT band is observed. The introduction of the methyl group into the cyclopropane fragment is accompanied by a decrease of ν_{CT} and in the presence of electron-accepting fluorine atoms in the three-membered ring ν_{CT} increases. Consequently, despite the specific electronic structure of cyclopropane and its derivatives[100], the nature of the influence of the substituents in the cyclopropane fragment (not containing the benzene ring—this case was examined above) on the position of the band in the spectra of the CTC of these compounds is the same as for the typical π-donors (benzene, naphthalene and ethylene derivatives).

Similar relations have been established also for the interaction of π- and σ-acceptors with saturated compounds of Group IVB metals: permethylpolysilanes[74–78], polygermanes[101], hexamethyldistannanes[101–103], and tetra-alkyl derivatives of germanium, tin, and lead[101,104,105]. Saturated tetra-alkyl monosilanes do not form complexes with TCE apparently as a consequence of the fairly high ionisation potential of the Si–C bond. However, it has been shown[106] that the marked distortion of the valence angles of the atoms involved in the formation of small rings with participation of silicon atoms leads to an appreciable decrease of the ionisation potentials of the corresponding monosilanes (the ionisation potential of 1,1-dimethyl-1-silacyclobutane is 9.4 eV compared with 10.5 eV for tetramethylsilanes[107]).

The silacyclobutanes –SiRR′ formed give rise to CTC with TCE and there is a linear relation between ν_{CT} and the sum of the inductive constants of the substituents R and R′ at the silicon atom

$$h\nu_{CT} = 2.38\ \Sigma\sigma_{IR,R'} + 3.56\ . \qquad (32)$$

Information about the d_π–p_π interactions has been obtained in the study of complexes of saturated silicon-containing sulphides R–S–R′ (XVIII) with TCE.[108] The attachment of silicon to the sulphur atom lowers the energy of the orbital occupied by the LEP of sulphur, which is manifested by hypsochromic shifts of the CT band and indicates the operation of the effect of the d_π–p_π interaction. This interaction breaks down when the silicon and sulphur atoms are separated by the $-CH_2$-fragment.

Electronic absorption spectroscopy of CTC has also been used to study the electronic structure of the silatranes

$RSi(OCH_2CH_2)_3N$ (XIX).[109–112]

5. Heterocyclic Compounds

In contrast to benzene derivatives, the electronic effects in the CTS of heteroaromatic compounds with an excess of π-electrons[113] have been less thoroughly investigated (see the review on the CTC of pyrrole derivatives[114]). A comparative study of the CTC of five-membered heterocycles with various π-acceptors[115,116] established that the π-donor capacity falls in the sequence pyrrole > furan ≥ thiophen and all the heterocycles are stronger electron donors than benzene. On the other hand, the stability of the CTC of benzene with TCE (the K_C constant) is higher, probably as a consequence of more favourable conditions for the mutual overlap of the orbitals.

Analysis of the values of ν_{CT} and K_C for thiophen, selenophen, and tellurophen[117,118] as well as photoelectron spectroscopic data (ionisation potentials) indicate unambiguously the π-character of the HOMO of thiophens. The π,σ-character of the CTC of thiophens with iodine is demonstrated by the different nature of the variation of the K_C for methyl-substituted thiophens and pyrroles. The K_C for the latter decrease in the sequence of substituents $3\text{-}CH_3 > 2\text{-}CH_3 > H > 2,6\text{-di-}CH_3$, which agrees with the increase of the steric hindrance around the reaction centre (the nitrogen atom). On the other hand, the K_C for the series of thiophens increase in the same sequence, which corresponds to the predominance of the electronic effects over steric effects. This is also indicated by the appreciably different equilibrium constants for the complex-formation reactions of thiophen (K_C = 0.61 mol^{-1}), pyridine (K_C = 160 mol^{-1}), and tetrahydrofuran (K_C = 315 mol^{-1}) with I_2.

It has been established that[118] the following relation holds for the CTC of thiophens and benzenes with TCE:

$$\lg K_c^t = 0.9 \lg K_c^b + 0.2\ . \qquad (33)$$

The slope, which is close to unity, indicates the similarity of the HOMO of the two classes of the compounds. A linear relation has also been established between $\lg K_C^t$ and the Hammett σ constants[118] (ρ_{CT} = 1.6). In the CTC with TCE, iodine, and chloranil the HOMO is of the mixed n,π-type.[11] On passing to 5,5-dimethyl-2,2-bithienyl the CTC are stabilised by the $+I$ effect of the methyl group. It follows from the K_C for bithienyl and methylthiophen that the conjugation of the two thiophen rings in 2,2-bithienyl increases the basicity of the donor to a greater extent than the $+I$ effect of two methyl groups.

It has been remarked that[120] examination of the intramolecular interactions of thiophen derivatives in CTC is important for the understanding of the mechanism of the adsorption of these compounds on silochrome in experiments on gas-adsorption chromatography. Furan and thiophen derivatives in CTC exhibit approximately the same electron-donating properties[115,116,118]. The fact that 2-phenylfuran is a stronger electron donor than furan confirms, according to Eittah and Hamed[121], the formation of CTC of the π,π-type. The low frequencies ν_{CT} indicate significant conjugation effects in 2-phenylfuran, which confirms indirectly the planar structure of this molecule. The conjugation effects

are enhanced on passing to 2,5-diphenylfuran, whose molecule is evidently also planar. The conclusion that phenylfurans have a quasi-rigid structure, reached on the basis of electronic spectrosopic data for CTC,[121] has been confirmed by quantum-mechanical calculations.

The intramolecular interactions in the CTC of organic and organoelemental derivatives of thiophen and furan have been investigated systematically[122–124]. The replacement of the methyl group in methylthiophen by the $Si(CH_3)_3$ group leads to an appreciable weakening of the electron-donating properties of the compound. Thus the effect of the d_π–p_π interaction, opposed to the $+I$ effect of the silyl groups, is characteristic of derivatives of thiophen as well as the derivatives of benzene, naphthalene, and ethylene discussed above. The electronic effects of the substituent in the CTS of thiophen derivatives have been compared with the electronic effects in the ground state (investigated by measuring the chemical shift τ using NMR data).[123] For a series of compounds, the values of τ and ν_{CT} are linearly related:

$$\tau\,(\text{p.p.m.}) = 6.30 - 0.00015\,\nu_{CT} \quad . \qquad (34)$$

The linear relation shows that the electronic effects of the substituents do not change fundamentally on passing from the ground to the charge-transfer state. The points corresponding to compounds with thienyl substituents deviate from relation (34) towards lower values of ν_{CT}, indicating an increase of the effect of the n,π conjugation of the substituents with the ring in the CTS (the $+E$ effect).

The observed relations are similar to those discussed above for benzene derivatives[26]. At the same time, in contrast to benzene derivatives, an increase of the degree of the d_π–p_π interaction between the 3*d* orbitals of the silicon atoms and the π electrons of the thiophen ring has been observed in the CTS of substituted thiophen. This effect is manifested only in the presence of two electron-accepting substituents in the thiophen ring. The values of ν_{CT} in the spectra of the CTC of organoelemental derivatives of thiophen and furan with TCE [122–124] indicate a diminution of the electron-accepting properties of the elements of the silicon subgroup in the sequence Si > Ge > Sn, which is analogous to that for derivatives of benzene and determined by the effect of the d_π–p_π interaction, which weakens on passing from silicon to tin.

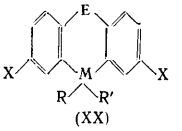
An analogy with benzene derivatives is also observed as regards the sharp enhancement of the electron-donating properties in the CTS of derivatives with substituents of the type $CH_2Si(CH_3)_3$, which is a consequence of the σ,π conjugation. The frequencies ν_{CT} of thiophen and furan derivatives are linearly related[124]:

$$\nu_{CT}^{t} = 0.46\nu_{CT}^{f} + 11000 \quad . \qquad (35)$$

The relation describes compounds with both organic and organoelemental substituents. Despite the lower ionisation potential of thiophen compared with furan[125], thiophen derivatives with electron-donating substituents [CH_3–, $C(CH_3)_3$–] have greater and not smaller frequencies ν_{CT} compared with their furan analogues. The reason for the inversion of the ν_{CT} in thiophen and furan derivatives is the greater sensitivity of the HOMO of furan derivatives to the influence of ring substituents[124]. According to some data[125,126], the sensitivity of the HOMO of aromatic compounds to the influence of substituents varies in the sequence furan > pyrrole > thiophen > benzene.

Derivatives of tetrathiafulvalene and tetrathiatetracene as well as certain other sulphur-containing heterocycles have attracted attention recently in connection with the discovery of conducting properties in their crystalline CTC and radical-ion salts[127,131]. These investigations established in particular[128] that the radical-ion salts derived from compounds in which there is a maximum charge transfer from the donor to the acceptor (tetracyanoquinodimethane) in liquid solution have high conductivities. Consequently the properties of molecular complexes in the liquid solution predetermine the conducting properties of the compounds formed from the given series of components in the solid phase.

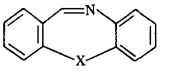
The spectra of the CTC of heterocyclic anthracene-like compounds of type (XX) have been investigated in a series of studies[132–134]:



(XX)

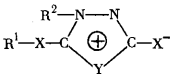
E = N — C_2H_5, O, S;
M = Si, Ge, Sn;
R, R′ = CH_3, C_6H_5, H .

The joint analysis of ν_{CT} data[133,134], the ionisation potentials[135], and the results of X-ray diffraction analysis[136,137] of these compounds has shown that the enhancement of the electron-donating properties takes place in parallel with the increase of the dihedral angle between the rings. The latter corresponds to an approach of the molecular skeleton to the planar structure and to an increase in the degree of conjugation in the sequences O < S < N and Sn < Ge < Si. As already mentioned, similar relations hold for phenylfurans[121]:



(XXI)

X = CH_2, O, S, NCH_3, C=O



(XXII)

X = O, S, $NCOR^1$, $NCSR^2$,
Y = O, S, NR^2, NH_2 .

The linear correlation between ν_{CT} and the ionisation potentials (electronic spectroscopic data for the CTC with CTE and photoelectronic spectroscopic data[138])

$$\nu_{CT} = (1.20 \pm 0.06)\ I_D - (6.3 \pm 0.5) \qquad (36)$$

has been established for derivatives of 11*H*-dibenzo[*b*,*f*]-azepine (XXI). The charge-transfer complexes of certain mesoionic compounds of type (XXII) have been investigated[139,140]. Analysis of the ν_{CT} data made it possible to assign the CTC of compound (XXII) with TCE to the π,π-type and to estimate the relative electron-donating capacities of the exocyclic groups in mesoionic heterocycles in the CTS.

III. PROSPECTS FOR THE APPLICATION OF THE ELECTRONIC EMISSION SPECTROSCOPY OF CHARGE-TRANSFER COMPLEXES

The application of the electronic absorption spectroscopy of the CTC to the study of intramolecular interactions is effective only on formation of comparatively stable complexes giving rise to a sufficiently intense CT band in the electron spectrum. The high sensitivity of the electronic emission spectroscopy makes it important for the study also of weak CTC. The following main applications are promising in this connection.

1. The study of the electronic emission spectra of the CTC formed in the ground state (a version which is the direct opposite of electronic absorption spectroscopy). The information thus obtained is important for the understanding of the nature of the donor–acceptor bonds[141–144]. For example, it has been shown[141,142] that the position of the CTC

emission band in the spectra of a series of benzene derivatives is determined directly by the ionisation potentials of the donors (for the same acceptor). However, overall, the electronic emission spectra of the CTC have not been as thoroughly investigated and described systematically as the electronic absorption spectra and this method has not therefore found extensive applications in physical organic chemistry.

2. Many more studies have been made (see, for example, the relevant reviews[145-147]) on the electronic emission spectra of the CTC formed only in an excited state (exciplexes) via the mechanism

$$^1D^* + A \rightleftharpoons (D^+A^-)^* \rightarrow D + A + h\nu_{CT}^{em} . \quad (37)$$

Numerous experimental data, starting with the work of Leonhardt and Weller[148], established a linear relation between the energy of the fluorescence maximum of the exciplex $h\nu_{exc}^{fl}$, the ionisation potential of the donor I_D, and the electron affinity of the acceptor E_A similar to Eqn.(5).

Apart from these two methods, the following two indirect procedures for the investigation of weak CTC, in which the quenching of the luminescence of one of the components of the complex due to the complex formation in the excited or ground state is considered, are also important.

3. The study of the influence of the formation of non-luminescent CTC in an excited state from luminescent components. This dynamic quenching process (of the second kind[157]) corresponds to the following scheme:

$$D^* + {}^1Q \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (DQ)^* \begin{cases} \xrightarrow{k_c} {}^1D + {}^1Q & (38) \\ \xrightarrow{k_{ict}} {}^3D^* + {}^1Q & (39) \end{cases}$$

(where Q is the molecule of the quenching agent) and its kinetics are described by the familiar Stern–Volmer equation[145]:

$$\varphi_0/\varphi = 1 + k_q\tau_0[Q] = 1 + K_q[Q] , \quad (40)$$

where ϕ_0 and ϕ are the luminescence quantum yield in the absence and presence of the quenching agent respectively, τ_0 is the lifetime of the excited state in the absence of the quenching agent (seconds), [Q] the molar concentration of the quenching agent, k_q the observed rate constant for the quenching of the luminescence (litre mol^{-1} s^{-1}), $K_q = k_q\tau_0$ the Stern–Volmer quenching constant (litre mol^{-1}), k_c the true rate constant for quenching in the complex (litre mol^{-1} s^{-1}), and k_{ict} the rate constant for the possible intersystem crossing (litre mol^{-1} s^{-1}).

For the majority of systems in solvents of low viscosity, k_q is of the order of magnitude of 10^9–10^{10} litre mol^{-1} s^{-1}, which is close to a diffusion-controlled constant $k_{dif} = 8RT/300\eta$, where R is the gas constant (J mol^{-1} K^{-1}), T the temperature (K), and η the viscosity (P). It can be shown[145] that the following relation can be derived for Scheme (38) or (39):

$$k_q = k_c k_1/(k_c + k_{-1}) . \quad (41)$$

For strong quenching agents, $k_c \gg k_{-1}$ and we obtain

$$k_q \cong k_1 \cong k_{diff} , \quad (42)$$

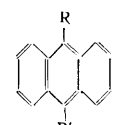
i.e. the quenching efficiency is determined exclusively by the diffusion of the species forming the intermediate complex. For a weak quenching agent ($k_c \ll k_{-1}$),

$$k_q = k_c k_1/k_{-1} = K_c k_c , \quad (43)$$

where K_C is the equilibrium constant of the complex formation process. In this case K_q is independent of the viscosity of the solution and should be determined by the donor–acceptor properties of the fluorophor and the quenching agent.

There have been a number of studies which have confirmed this hypothesis. Thus the quenching of the fluorescence of naphthalene derivatives by carbon tetrachloride and dimethylaniline has been investigated[149]. In the first case the quenching rate constant k_q diminishes from 1.3×10^{10} litre mol^{-1} s^{-1} for 1-methoxynaphthalene to 1.3×10^7 litre mol^{-1} s^{-1} for 1-cyanonaphthalene; on the other hand, in the second case the quenching rate constant increases from 5.7×10^7 to 2.8×10^9 litre mol^{-1} s^{-1}. This indicates different donor–acceptor natures of the naphthalene derivatives: they behave as electron acceptors in the complexes with CCl_4 and as electron donors in the complexes with $NH(CH_3)_2$. Such reversal of the donor–acceptor nature of the quenching mechanism has been observed in the benzonitriles–anisoles[150] and benzophenones–substituted benzenes[151] systems.

The problem has been studied in detail in relation to the quenching of 9- or 9,10-substituted anthracenes (An) by various substances[152-155]:



(XXIII)

For the quenching of An having the general formula (XXIII) by triphenylphosphine (Pp), linear correlations have been established between the logarithm of k_q and the σ constants of the substituents, the values of ρ for compounds with electron-accepting and electron-donating substituents being 0.55 and 3.34 respectively. The positive sign of ρ shows that the quenching takes place in the complex $\overset{+}{An}Pp$ and that the quenching process is more sensitive to structural changes in the molecules for all electron-donating substituents. Analogous data have also been obtained using *N*,*N*-dimethylaniline as the acceptor. On quenching of anthracenes (XXIII) by tris(pentafluorophenyl)phosphine (PPp),[155] the opposite relation is observed: the Hammett correlations $\lg k_q \propto \sigma$ have negative reaction constants: $\rho = -1.15$ for compounds with electron-accepting substituents and $\rho = -0.78$ for compounds with electron-donating substituents. Consequently the quenching takes place via the complex $\overset{+}{An}PPp^-$. Whereas in the quenching of the naphthalene derivatives by acetyl chloride in a liquid solution the quenching efficiency (the Stern–Volmer constant) increases with decrease of the ionisation potentials of the naphthalene derivatives[158], in the quenching of polycyclichydrocarbons by tetracyanoethylene in a liquid solution the process is controlled by diffusion[159]. The quenching of the fluorescence of the acridinium ion (acceptor) by alkyl and aryl bromides and iodides (donors) probably[160] proceeds via the formation of an exciplex [see Scheme (39)], i.e. constitutes an intersystem crossing. In the case of quenching agents with ionisation potentials I_D less than 8.7 eV the process is controlled by diffusion, in accordance with Scheme (42). For $I_D > 8.7$ eV, the quenching proceeds via a charge-transfer complex, in conformity with Scheme (43). The dependence of the free energy of formation of the exciplexes on the donor–acceptor properties of the components has been examined[161,162].

4. The study of the influence of the formation of non-luminescent complexes in the ground state on the luminescence of the components:

$$^1D + {}^1Q \overset{K_c}{\rightleftarrows} {}^1(DQ) . \quad (44)$$

For many problems in physical organic chemistry (particularly for the study of intramolecular interactions), this case (quenching of the first kind[157]) is of special interest. The literature data on this problem are extremely limited and refer mainly to liquid solutions.

According to Parker[163], quenching of the first kind is described by the Stern–Volmer equation, but the quenching constant K_Q represents the equilibrium constant of the complex formation process (44). The experimental quenching constants in this case as a rule exceed the equilibrium constants determined from the absorption spectra[164–170]. Positive deviations from the linear Stern–Volmer equation are then observed and the experimental curve is described satisfactorily by the equation[164,168–170]

$$\varphi_0/\varphi = (1+K_q[Q])(1+K_Q[Q]) \quad , \qquad (45)$$

where K_q is the constant of the dynamic quenching process (of the second kind) and K_Q is the constant of quenching of the first kind, i.e., according to Parker, the equilibrium constant for the complex formation process.

The validity of Eqn.(45) implies that two quenching mechanisms—of the first and second kinds—operate simultaneously in liquid solutions. It has been shown[170] in relation to the quenching of chlorophyll and its derivatives by aromatic nitro-compounds that the contribution of the quenching of the first kind increases as the donor–acceptor bonds are strengthened. The complex picture of the luminescence quenching process involving CTC described above hinders the application of this method to the study of weak complexes in the ground state and intramolecular interactions. However, this possibility appears when the luminescence is quenched as a consequence of the formation of complexes in the ground state in a low-temperature matrix, where the diffusion of molecules is eliminated and only the mechanism of the quenching of the first kind operates. This case has been examined in a study[171] where a linear relation between the logarithm of the Stern–Volmer quenching constant and the charge-transfer frequencies in the absorption spectra of the CTC has been found for the quenching of naphthalene derivatives by TCE at 77 K:

$$\ln K_Q \cdot 10^{-4} = -7.40\ \nu_{CT} + 14 \quad . \qquad (46)$$

In addition, a linear correlation has also been established between K_Q and K_C [the equilibrium constant of the complex formation reaction between naphthalene derivatives and TCE at 298 K (the Benesi–Hildebrand method)]:[172]

$$K_Q \cdot 10^{-4} = (2.16 \pm 0.22)\ K_c + (0.49 \pm 0.33) \quad , \qquad (47)$$

the fact that $K_Q \neq 0$ is obtained for $K_C = 0$ (the absence of complex formation in the ground state) being possibly associated with the presence of contact complexes in solution.

The method for the investigation of complex formation described above, which can be referred to as static quenching of luminescence of the first kind, can be used when (a) the linear Stern–Volmer relation holds in the working range of the concentrations of the quenching agent and (b) there is a linear relation between the logarithms of the quenching constant (or in a special case between the constants themselves) and the donor–acceptor characteristics of the substances—fluorophors or quenching agents (ionisation potentials, electron affinities, σ constants, charge-transfer frequencies, etc.). Subject to tests of the validity of the given conditions, the method has been used to investigate complex formation on the ground states of indigo–π-acceptors[173] and organometallic compounds–oxygen (or t-butyl peroxide) systems[174–176]. In the latter case valuable information was obtained about the intramolecular interactions in organomercury compounds.

* * *

Thus electronic absorption and emission spectroscopies are informative methods for the investigation of intramolecular interactions in the molecules of the species involved in charge-transfer complexes and of the characteristics of complex formation in general. The information thus obtained is important not only for the study of the mutual influence of atoms in organic and particularly organoelemental compounds (the facts concerning this field have been vigorously accumulated and treated systematically) but also for the establishment of empirical relations between the structures and reactivities of compounds and for the modelling of primary reactions in complex chemical transformations. In the latter instance, particularly for the recording of weak complexes of organoelemental compounds, emission spectroscopy in low-temperature matrices is extremely promising.

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