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Degree of Charge Transfer in Donor-Acceptor Systems of the $\pi-\pi$ Type

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The principal methods for the determination of the degree of charge transfer are examined and experimental data on the intermolecular distribution of electron density in charge-transfer complexes and radical-ion salts of the $\pi-\pi$ are surveyed. The relation between the degree of charge transfer and the ionisation potential of the donor, the half-wave potential in the anodic oxidation of the donor, and the electron affinity and the polarographic reduction potential of the acceptor, which largely determine the degree of charge transfer in donor-acceptor systems of the $\pi-\pi$ type, is discussed.
The bibliography includes 104 references.

CONTENTS

I. Introduction 334
II. Degree of charge transfer and methods for its determination 334
III. Theoretical ideas concerning the dependence of the degree of charge transfer on the characteristics of the system components. 338
IV. Experimental data 338
V. Conclusion 340

I. INTRODUCTION

The interaction of a π-electron donor with a π-electron acceptor is accompanied by an intermolecular redistribution of electron density. All the properties of the system as a whole depend on the effectiveness of this process, which is characterised by the degree of charge transfer (CT). Weak $\pi-\pi$ complexes exhibit semiconducting and photoconducting properties.[1-3] Systems with a degree of CT within the limits 0.4–0.7 frequently behave as organic metals, while a further increase of the degree of CT again leads to a semiconductur.[6-13] The degree of CT should therefore be regarded as one of the most important characteristics of the donor–acceptor system.

The main textbooks and reviews on donor–acceptor interaction[14-19] include only fragmentary data on the determination of CT in systems of the $\pi-\pi$ type. Theoretical ideas concerning the laws governing the variation of the degree of CT are considered in the present review for the first time and the experimental data on systems of the $\pi-\pi$ type which have accumulated are also discussed.

II. DEGREE OF CHARGE TRANSFER AND METHODS FOR ITS DETERMINATION

According to Mulliken,[15] the behaviour of a donor–acceptor system can be described by the following wave function:

$$(D, A) \quad (D^+ - A^-)$$

where ψ_0 is the wave function of a hypothetical structure in which only the van der Waals interaction obtains and ψ_1 the wave function of a hypothetical "dative" structure in which one electron has been transferred from the donor to the acceptor and there is a semipolar bond between the donor and the acceptor, but it need not necessarily be of the localised interatomic type. An increase of the fraction of electron density transferred from the donor to the acceptor corresponds to an increase of the coefficient b. The quantitative characteristic of this process is the resulting charge or degree of CT (δ). The degree of CT is expressed[15] as $\delta = b^2 + abS_{01}$, where S_{01} is the overlap integral of the wave functions ψ_0 and ψ_1. Some workers define the degree of CT as b^2 or $b^2/(a^2 + b^2)$,[14] which leads to results in agreement with Mulliken's approach[15] only for very low values of δ.

Thus Mulliken's approach is based on the idea of a partial charge transfer: the real system is assumed to be, as it were, made up of two extreme structures. An analogous interpretation follows from the calculation for the intermolecular complex as a "supermolecule" by the LCAO-MO method.[20-29] As a consequence of the formation of molecular orbitals delocalised over the entire supermolecule, an intermolecular charge distribution takes place and partial resultant charges arise on both the donor and the acceptor. In the determination of this resultant charge, the same difficulties arise as in the determination of atomic charges in calculations for the usual molecules.

A different model is frequently used to describe the properties of crystalline donor–acceptor systems. According to this model, the donor–acceptor system represents a mixture of real donor–acceptor pairs with zero and total charge transfer. The degree of CT or the amount of ionic character is defined as the ratio of the number of pairs with total charge transfer to the total number of donor–acceptor pairs.[6] Although this model differs fundamentally from the previous ones, as regards numerical values it apparently yields the same results as Mulliken's model.

The method of dipole moments, nuclear quadrupole resonance (NQR), X-ray electronic spectroscopy (XES), infrared spectroscopy (IR), Raman spectroscopy (RS), and quantum-chemical calculations are usually employed to determine the degree of CT.[6,14,16,20] The method dipole moments is one of the main ones and has been considered in detail.[16] The dipole moment is a general characteristic of the complex, characterising the charge distribution over the complex as a whole. The experimenqally determined dipole moment of the complex is ususally regarded as the vector sum of the dipole moments of the donor, the acceptor, and the donor–acceptor bond (with a specified geometry of the complex). However, the formation of the complex may be accompanied by a change in the dipole moments of the components and can be also complicated by the formation of complexes of different geometry; this greatly hinders a correct estimation of the dipole moment of the donor–acceptor bond in the study of complexes with a slight degree of CT. The application of the method of dipole moments to the study of weak $\pi-\pi$ complexes is therefore coupled with considerable difficulties.[16,30]

In contrast to the dipole moment method, the NQR method[20] yields information about the local distribution of valence

electrons at the sites where nuclei with a quadrupole moment are located, which must be regarded as a major advantage of the NQR method. However, an exact interpretation of the experimental resonance frequency shifts is not always possible, since the quadrupole interaction constants depend not only on the distribution of valence electrons but also on the contribution by the remaining electrons of the atom involved in resonance, on the degree of hybridisation, on the influence of the crystal field, and on the thermal movement of the molecules. For low degrees of CT, the last effects in fact predominate; analysis of the experimental data obtained in a study of weak $\pi-\pi$ complexes by the NQR method has shown[31] that the influence of the CT on the resonance frequency shift can be fully swamped by the crystal field effects. It is therefore virtually impossible to obtain the quantitative characteristics of the degree of CT for weak complexes by the NQR method.[32]

X-Ray electronic spectroscopy is based on the parallel variation of the effective charges of the atoms investigated and of the shift of their lines in the X-ray electronic spectrum or on the characteristic change in band shape.[33] The principles of the method have been considered in fair detail by Poleshchuk and Maksyutin[20] and Ikemoto et al.[33] One must note that information about the redistribution of valence electrons on complex formation is obtained in this instance from the change in the ionisation potential of the inner electrons, whose ionisation is accompanied by an appreciable reorganisation of the electron shell. Since the decrease of the energy of the ion as a consequence of the reorganisation of the electron shell can exceed by an order of magnitude the change in the ionisation potential due to the redistribution of valence electrons, the interpretation of the experimental data may prove to be very difficult. In practice, this problem is solved by means of a preliminary study of a series of related complexes in which the degree of CT is known beforehand. However, it is clear that the XES method is relatively unsuitable for the study of complexes with an insignificant degree of CT and complications can also arise in the investigation of donor–acceptor systems with a considerable charge transfer.

The IR and Raman spectroscopic methods have not so far found extensive applications in the determination of the degree of CT. IR spectroscopy is used in the study of $\pi-\pi$ complexes as a rule only for the qualitative investigation of the characteristics of the structure of the complex, i.e. it helps to establish whether the intermolecular associated species investigated is a true charge transfer complex (CTC) or a radical-ion salt, whether proton transfer takes place, etc.[14–17,34–40] This is due to the fact that the changes observed in the IR spectra on passing from a weak complex to a radical-ion salt are much more significant than the differences between the spectra of the isolated components and the weak complex or between the spectra of two different weak complexes. However, even the formation of weak $\pi-\pi$ complexes leads to the observation of a number of changes in the spectra,[40] which carry information about the electronic structure of the CTC. Since IR spectroscopy as a method for the determination of the degree of CT has not yet attracted the attention of investigators which it deserves, we believe it necessary to consider in somewhat greater detail the characteristic features of the IR spectra of the CTC.

On formation of the CTC, the following changes may be observed in the IR spectra: the appearance of "forbidden" vibrations of the donor and acceptor and of new vibrations of the donor–acceptor bond and also a spectral shift and a change in the integral intensities of the allowed vibrations of the donor and acceptor.

The appearance of forbidden vibrations of the components in the IR spectrum of the complex is not frequently observed.[41] One of the instances thoroughly investigated in this respect is the CTC of tetracyanoethylene.[42–45] A band appears in the IR spectrum of the hexamethylbenzene–tetracyanoethylene CTC at 1561–1565 cm^{-1}, which is due to the $A_{1g}\nu(C=C)$ vibrations of tetracyanoethylene. The study of polarised IR spectra of the CTC single crystal showed that these vibrations are active when the electric field vector of the polarised radiation is directed at right angles to the planes of the donor (D) and acceptor (A) molecules along the alternating DADA stack.[42,45]

This conclusion is satisfactorily consistent with the Ferguson–Person–Friedriech model,[46] which envisages a delocalisation effect on the oscillation of the charge in the direction of charge transfer during vibrations in the plane of the donor or acceptor molecules. In the case of the 2:1 hexamethylbenzene–tetracyanoethylene CTC, two new bands appear in the IR spectrum (at 1567 and 1295 cm^{-1}), polarised at right angles to the planes of the donor and acceptor molecules. The latter band refers in all probability to the fully symmetrical vibrations of the $C(CH_3)$ group of hexamethylbenzene. In the spectra of the hexamethylbenzene–hexacyanobenzene, phenanthrene–hexacyanobenzene, and 1,3,5-trimethoxybenzene–hexacyanobenzene complexes, a new band appears at 1300 cm^{-1} and is apparently due to the $A_{1g}\nu(C-C)$ vibrations of hexacyanobenzene, which are manifested in the Raman spectra at 1310 cm^{-1}.[47]

Table 1. The shifts of the A bands in the IR or Raman spectra on formation of CTC.

Donor	Acceptor	ν, cm^{-1}	$\Delta\nu$, cm^{-1}	Assignment	Refs.
Pyrene	BQ	1655	−5	ν_{CO}	[50]
Hydroquinone	"	3063	−1	ν_{CH}	[51]
"	"	1654	−21	ν_{CO}	[51]
"	"	3250	0	ν^{*}_{OH}	[51]
"	"	1357	−97	ν^{*}_{COH}	[51]
Hexamethylbenzene	TCNE	1557	−5	ν_{CC}	[52]
"	"	2228	−3	ν_{CN}	[52]
"	"	1564	−16	ν_{CC}	[53]
"	"	2230	−7	ν_{CN}	[53]
p-Xylene	"	1564	−6	ν_{CC}	[53]
"	"	2230	−7	ν_{CN}	[53]
Mesitylene	"	1564	−4	ν_{CC}	[53]
"	"	2230	−3	ν_{CN}	[53]
Anisole	"	1564	−8	ν_{CC}	[53]
"	"	2230	−3	ν_{CN}	[53]
o-Dimethoxybenzene	"	1564	−9	ν_{CC}	[53]
"	"	2230	−3	ν_{CN}	[53]
Pyrene	"	2230	−10	ν_{CN}	[53]
o-Phenylenediamine	TCNQD	2223	−13	ν_{CN}	[54]
Hexamethylbenzene	CA	1659	−12	ν_{CO}	[55]
"	"	1572	−11	ν_{CC}	[55]
"	"	1112	−2	ν_{CCl}	[55]
Pyrene	TNB	1340	−5	ν_{NO_2}	[56]
Anthracene	"	1546	−4	ν_{NO_2}	[56]
"	"	1360	−5	ν_{NO_2}	[56]
Perylene	"	1546	−4	ν_{NO_2}	[56]
Naphthalene	"	1546	−6	ν_{NO_2}	[56]
"	"	1360	−8	ν_{NO_2}	[56]
Hexamethylbenzene	"	1546	−6	ν_{NO_2}	[56]
"	"	1360	−9	ν_{NO_2}	[56]
1,2-Benzoperylene	"	1546	−2	ν_{NO_2}	[56]
1,2,5,6-Dibenzanthracene	"	1546	−2	ν_{NO_2}	[56]
Toluene	TCNQD	2223	−1	ν_{CN}	[57, 58]
o-Xylene	"	2223	−2	ν_{CN}	[57, 58]
Veratrol	"	2223	−2	ν_{CN}	[57]
1-Methoxynaphthalene	"	2223	−3	ν_{CN}	[57]
Naphthalene	"	2223.5	−3.5	ν_{CN}	[58]
2,6-Dimethylnaphthalene	"	2223.5	−2.5	ν_{CN}	[59]

Notation: ν are the frequencies of the vibrations of the corresponding groups in the "free" donor or acceptor; $\Delta\nu$ are the shifts on complex formation. BQ = 1,4-benzoquinone, TCNE = tetracyanoethylene, TCNQD = 7,7,8,8-tetracyanoquinodimethane, TNB = *sym*-trinitrobenzene, and CA = *p*-chloranil.

* Vibrations of the functional groups of the donor; in all the remaining cases the vibrations are those of the corresponding groups of the acceptor.

Few studies have been devoted to the intermolecular D–A vibrations[41] despite the fact that they might yield information about both the strength of the D–A bond and about the degree of CT. This is apparently due to the difficulty of the experimental measurement of absorption bands in the region of 100 cm^{-1} and of the interpretation of the results. For example, a band has been observed at 115 cm^{-1} in the spectrum of the mesitylene–tetracyanoethylene CTC in solution in the donor and was assigned to intermolecular vibrations.[48] Later doubts arose about the correctness of this assignment, since intramolecular vibrations of the acceptor are manifested in this region of the spectrum.[41] More extensive studies on tetracyanoethylene complexes have been carried out by Rossi and Haselbach,[49] who concluded that intermolecular vibrations are indeed observed in the range 80–100 cm^{-1}. Both the forbidden vibrations and the D–A vibrations carry information about the degree of CT, but the use of this information for the determination of the degree of CT has not so far been reliably achieved.

Spectral shifts of the allowed absorption bands of the CTC components are almost always observed on formation of crystalline CTC. The magnitude of the shift of the vibrational bands does not then ususally exceed 5–10 cm^{-1} (Table 1) and amounts to more than 20 cm^{-1} only on formation of radical-ion salts.[60]

It is noteworthy that the spectral shift on complex formation has been used by some workers for a kind of classification of donor–acceptor systems. For example, it has been suggested[61] that all the CTC derived from *p*-benzoquinone can be divided into three types depending on the shift of the ν(CO) and ν(CC) stretching vibration bands.

Theoretical ideas about the influence of complex formation on IR spectra have been developed on the basis of several models.[14,15,41,62] At present there is no generally accepted theory taking into account the influence of both the "classical" forces and the CT forces on the spectroscopic parameters of the complex. According to Mulliken's theory,[15] intermolecular charge transfer should be accompanied both by a shift of the allowed bands in the IR spectrum and by a change of their integral intensity. If the band shifts are insignificant, then the relation between $\Delta\nu$ and the degree of CT (δ) is described by the equation:[15,58]

$$\delta = \frac{2\Delta\nu}{\nu_0}\left[1 - \frac{\nu_1^2}{\nu_0^2}\right]^{-1} , \qquad (1)$$

where ν_0 and ν_1 correspond to the positions of the band investigated in the spectra of the "free" component and its radical-ion respectively. It has been shown experimentally that in the case of the TCNQD complexes [there is a shift of the ν(CN) band], for example, Eqn.(1) assumes the following form:[58,59]

$$\delta = 43.5 \cdot \Delta\nu/\nu_0 . \qquad (2)$$

A corresponding equation has been obtained in another study[60] from the experimental band shifts in the spectra of CTC and radical-ion salts with a comparatively high degre of CT known beforehand:

$$\delta = \Delta\nu/44 . \qquad (3)$$

Eqns.(2) and (3) lead to close results, although the degree of CT obtained from Eqn.(2) is lower by 12%. This suggests that the approximation in the form of Eqn.(1) is fairly well-founded and the equation can be used to calculate the degree of CT in other donor–acceptor systems, for example, in a tetracyanoethylene complex.[63] Using the literature data,[64–69] it is possible to obtain equations for the calculation of the degree of CT from the shift of the CO vibration bands in the spectra of the CTC of *p*-benzoquinone and 2,3-dibromo-5,6-dicyano-*p*-benzoquinone:

$$\delta = 11.2 \cdot \Delta\nu/\nu_0 ,$$
$$\delta = 16.6 \cdot \Delta\nu/\nu_0 .$$

The influence of complex formation on the integral intensities of the stretching vibration bands is in the general case more complex.[15] The band intensity is determined by the so-called "$M_{0,1}$ term" which depends both on the change of the dipole moment μ_N and on the "delocalisation" moment M_d, i.e. on the vibronic interactions:

$$M_{0,1} = \partial\mu_N/\partial Q_i + M_d .$$

The quantity M_d may differ from zero if the following parameters change as a consequence of the vibrations investigated: the intermolecular donor–acceptor distance, the ionisation potential, the electron affinity, or the overlap integral S_{01}. If the vibrations investigated do not entail such changes, then $M_d = 0$. The term $M_{0,1}$ may be expressed by the dependence on the dipole moments of hypothetical "without bond" and "dative" structures:[15,57]

$$\delta = \frac{A_N^{1/2} - A_0^{1/2}}{A_1^{1/2} - A_0^{1/2}} , \qquad (4)$$

where A_N, A_0, and A_1 are the integral intensities of the stretching vibrations studied in the spectra of the complex, the hypothetical structure "without bond", and the "dative" structure respectively. If one studies, for example, the stretching vibrations of the acceptor, then A_0 and A_1 should be approximately equal to the integral intensities of the bands due to the given vibrations in the spectra of the "free" acceptor and its radical-anion respectively.[57–59]

It has been suggested[57–59] that Eqn.(4) can be almost always used in the study of the asymmetric vibrations of functional groups in the plane of the donor or acceptor in complexes of the $\pi-\pi$ type, since this should entail virtually no changes in the ionisation potential, the electron affinity, the donor–acceptor distance, and S_{01}. The validity of this hypothesis has been confirmed by the results of a study of single crystals of donor–acceptor systems using polarised infrared radiation.[45,55] It was established that the allowed stretching vibrations remain polarised in most cases virtually only in the plane of the component molecules of the CTC; consequently the contribution of the delocalisation moment is indeed insignificant. The stretching vibrations of the CO and CN groups in the CTC of quinones and tetracyanoethylene respectively belong to the above type.[45,55] On the other hand, certain vibrations involving the entire electronic system of the acceptor are polarised also along the DADA stack—for example, the CC vibrations in the 1,4-chloranil molecule (band at 1245 cm^{-1}).[45]

A change in the intensities of the bands due to allowed vibrations of the CTC components has been noted in a number of studies and has been used to investigate the CTC of σ-acceptors.[41] On the other hand, in the case of $\pi-\pi$ complexes the change in the intensities of the allowed vibration bands of the components has so far been used only in a few instances,[56–58,61] although it has been noted in a series of studies that this change is associated with CT from the donor to the acceptor.[45,47,55] It has been established[57] that the change in the integral intensities of the stretching vibration bands of the cyano-groups in the TCNQD spectrum is a more sensitive parameter than the spectral shift and an expression has also been obtained for the calculation of the degree of CT:

$$\delta = \frac{A_N^{1/2} - A_0^{1/2}}{2.8} . \qquad (5)$$

Eqn.(5) has been used to determine the degree of CT in both two-component donor–acceptor systems and in three-com-

ponent donor–acceptor–solvent systems.[57–59] The influence of the universal intermolecular interactions on the spectroscopic properties of the acceptor has been taken into account by studying under the same conditions a model compound which does not form CTC. The data thus obtained agree well with the results secured by other methods.

Among the methods for the determination of the degree of CT, mention should also be made of X-ray diffraction analysis (XDA) and electronic absorption spectra (EAS). The use of the XDA method is based on the characteristic changes in the geometry of the acceptor or donor when a neutral compound is converted into its radical-ion.[70–72] The EAS method is based on the measurement of the integral intensities of the CT bands in the ultraviolet absorption spectra:[14,73–75]

$$b^2 = \frac{f}{1.085 \times 10^{11} h\nu_{CT} R_{DA}^2},$$

where f is the oscillator strength of the electronic transition, $h\nu_{CT}$ the CT energy (cm^{-1}), and R_{DA} the intermolecular distance (cm). This equation has been used to determine the degree of CT[14,15,73–75] from the electronic spectra of various complexes in solutions and in the crystalline state (it is essential to take into account the change in f on passing to the crystalline state). The EAS method apparently yields reliable results in the study of CTC with a low degree of CT, for which the energy of the local transitions in the CTC components differs sufficiently from the CT energy.

Electronic spectroscopy can be used to determine the degree of CT from the shfit of the CT band maxima on changing the solvent.[76]

Apart from the methods for the determination of the degree of CT mentioned above, others are also used,[77,78] among which mention should be made of the elastic scattering of neutrons[79] and the measurement of the temperature dependence of the magnetic susceptibility.[80]

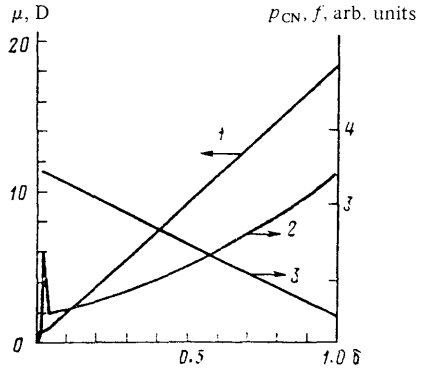


Figure 1. The calculated dependence of the dipole moment μ (line *1*), the oscillator strength f (line *2*), and the CN bond order P_{CN} (line *3*) on the degree of CT for model 7,7,8,8-tetracyanoquinodimethane complexes.[21]

The accuracy and reliability of the above methods are fairly difficult to estimate. Nevertheless, the results of calculations for the model complexes of 7,7,8,8-tetracyanoquinodimethane by the LCAO-MO method in the CNDO/S valence approximation give rise to the possibility of such analysis.[21] Fig.1 shows that the results of the calculation confirm the extremely high sensitivity of the dipole moment method. One should note that the z component of the dipole moment (the selected geometry of the complex is characterised by the fact that the donor has been displaced relative to the acceptor along the C_{2v} axis) is directly proportional to the degree of CT throughout the region. The overall dipole moment of the complex may differ from zero also in the absence of CT; one must therefore assume that the dipole moment method can be used with a high degree of accuracy for the study of complexes in which the degree of CT exceeds 0.03. Fig.1 shows that the EAS method based on the measurement of the integral intensities is probably comparatively unreliable. Its application is justified only in those cases where it is known that the transition accompanied by charge transfer does not interact with electronic transitions of another type.

One must assume that IR spectroscopy is a reliable method for the determination of the degree of CT, since, throughout the entire range of variation of the degree of CT, an approximately linear relation is observed between the degree of CT and the order of the bonds formed by the cyano-groups of the acceptor (Fig.1). However, one must note that this method can be used successfully only in those cases where the degree of CT exceeds 0.03, since the bond order hardly changes when δ varies in the range 0.01–0.03.

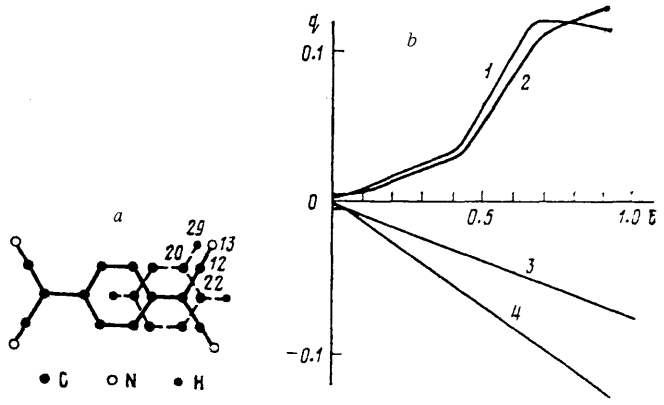


Figure 2. The selected geometry of the complex (*a*) and the dependence of the effective charges q on the individual donor atoms [1) C(20); 2) H(29)] and acceptor atoms [3) N(13); 4) C(7)] (*b*) on the degree of CT for model 7,7,8,8-tetracyanoquinodimethane complexes (calculation by the LCAO-MO method).[21]

Extremely interesting results have been obtained by comparing the degree of CT with changes in charge density on individual atoms of the charge-transfer complex. It was found that the relation between the characteristics investigated is not described in all cases by a simple linear equation (Fig.2). One should also note that in the region of weak CTC ($\delta < 0.05$) the changes in charge density are insignificant and may even prove to be the opposite to those expected [for example, the charge density on the C(22) atom of the donor increases slightly with decrease of δ]. It is therefore clear that all the methods for the determination of the degree of CT based on the measurement of parameters depending on the charge density on individual atoms can be used only for $\delta \geq 0.03–0.05$. The possibility of a non-linear relation between δ and q makes it necessary, in its turn, to treat

the results obtained by these methods with a certain amount of caution at least in those cases where the experimental determination of the above relation has not been carried out for a sufficiently large number of examples in which the degree of CT was known beforehand.

Thus, one must conclude that the dipole moment and IR spectroscopic (and also RS) mrthods are the simplest and most reliable, but apparently there is as yet no reliable method for the determination of the degree of CT for $\delta \leqslant 0.03$.

III. THEORETICAL IDEAS CONCERNING THE DEPENDENCE OF THE DEGREE OF CHARGE TRANSFER ON THE CHARACTERISTICS OF THE SYSTEM COMPONENTS

Mulliken's theory[15] yields several simple approximate equations describing the dependence of the degree of CT on the difference between the ionisation potential of the donor I_D and the electron affinity of the acceptor EA. Among them, mention should be made of the equation

$$\delta^{1/2} \simeq b \simeq \frac{CS_{01}}{I_D - EA - E_c}, \qquad (6)$$

where C is a constant for the CTC of the given type and E_C the energy of the Coulombic interaction of the oppositely charged species in the excited state of the (D^+, A^-) complex ($E_C \cong 3$–3.3 eV).

The following expression can also be obtained from Mulliken's theory:[15]

$$\left[\frac{1-\delta}{\delta}\right]^{1/2} \simeq -\frac{1}{\beta_0}(I_D - EA) + \frac{E_c}{\beta_0}, \qquad (7)$$

according to which the comparatively simple function of δ is approximately linearly related to the difference $I_D - EA$.

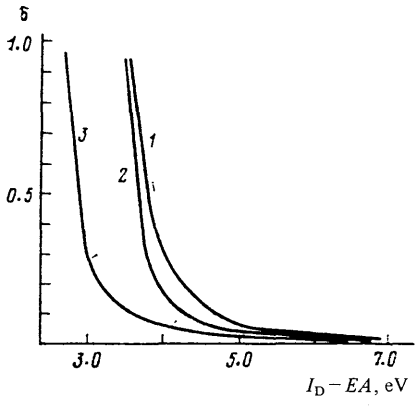


Figure 3. Dependence of the degree of CT on the difference between the ionisation potential of the donor and the electron affinity of the acceptor according to Mulliken's theory [1) $c^2S_{01} = 0.1$, $E_C = 3.2$ eV; 2) $c^2S_{01} = 0.16$, $E_C = 3.2$ eV] and the molecular orbital method in the CNDO/S valence approximation (curve 3).[21]

Although the above equations describe fairly satisfactorily the behaviour of a real system only for a comparatively small degree of charge transfer, they can be used successfully for a preliminary study of the dependence of the degree of CT on the characteristics of the CTC components (Fig.3).

Fig.3 also illustrates a relation obtained in calculations for model complexes,[21] which is represented by a function of the difference between the energies of the frontier molecular orbitals of the complex. Evidently Eqn.(6) and calculations by the LCAO-MO method predict the existence of a range of critical values of the difference $I_D - EA$, in which a comparatively sharp transition from the CTC to the radical-ion state should be observed.

Initially examination of this relation for mixed DADA stacks in the crystalline state[81–83] led to somewhat different results, according to which there exists not a critical region but a critical value of the difference $I_D - EA$ for which an abrupt transition to the radical-ion state should be observed. However, it has been shown[6,84] that a sharp increase of the degree of CT also in the crystalline state takes place likewise over a specific range of values of the above difference (Fig.4). It has been noted[6] that this range is in fact of greatest practical interest.

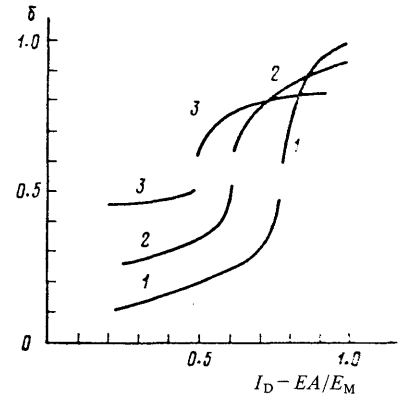


Figure 4. Characteristic form of the dependences of δ on $I_D - EA/E_M$ for different ratios β/γ (β and γ are the resonance and Coulombic integrals respectively): 1) 0.1; 2) 0.3; 3) 0.5.[6]

In crystals consisting of individual alternating stacks of D and A, the degree of CT is also not always unity.[6,83] For the majority of the complexes considered, the state of the system is described by the expression $E(\delta) = E_M(\delta) + (I_D - EA)\delta$, where E_M is the Madelung energy. Other conditions being equal, this should lead to approxomately the same dependence of δ on the difference $I_D - EA$ as that illustrated in Fig.4.

IV. EXPERIMENTAL DATA

The majority of the experimental determinations of the degree of CT available at present for donor–acceptor systems of the π–π type both in solutions and in the crystalline state are listed in Table 2. It follows from these data (Fig.5) that the experimental results agree satisfactorily with the theoretical predictions (Fig.3). The fairly considerable scatter of the experimental points is due to the experimental errors in the determination of I_D and EA and also to the approximate nature of the equations (which do not take into account the changes in S_{01}, E_C, and E_M on passing from one donor–acceptor system to another). Despite this, it is seen

from Fig. 5 that the transition from weak CTC to a state with almost total CT does not take place abruptly but in a certain transition region in the range $3.8 \leqslant I_D - EA \leqslant 4.3$ eV. The region $3.5 \leqslant I_D - EA \leqslant 4.1$ eV corresponds to donor-acceptor systems with the properties of quasi-one-dimensional metals, since these systems are characterised by a considerable but not complete CT.

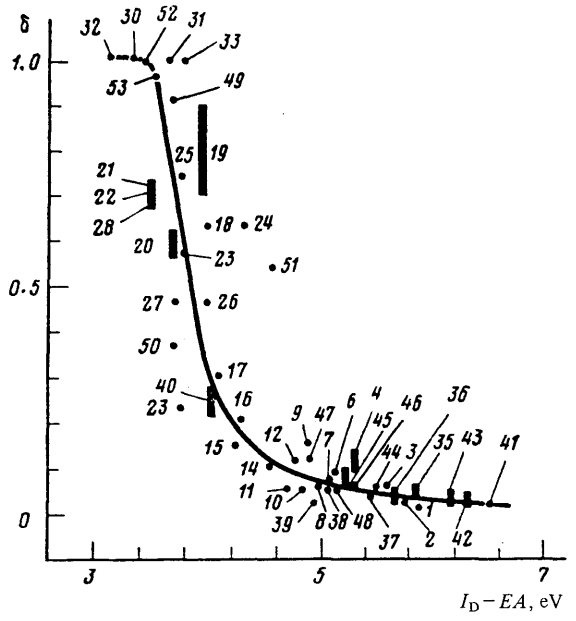


Figure 5. Dependence of the experimental values of δ on the difference $I_D - EA$. The ionisation potentials were taken from Refs. 94–97 and the electron affinities from Ref. 98; the numbering of the points corresponds to the numbering of the complexes in Table 2.

Apparently not only electrophysical characteristics but also the crystal structure is controlled in a definite manner by the degree of CT. It has been noted[99] that, on passing from one range of degrers of CT to another, a change in the method of packing is also observed. Indeed, donor–acceptor systems with $0.3 < \delta < 0.7$ consisting of mixed stacks are virtually unknown (according to Kistenmacher,[100] the dibenzotetrathiafulvalene–TCNQD complex is a system of this kind); systems with $\delta < 0.2$ consisting of individual stacks of the donor and acceptor species have not been observed either. All the foregoing findings suggest that the determination of fairly exact relations between the degree of CT and the characteristics of the system components, on the one hand, and between the degree of CT and chemical, spectroscopic, and photo- and electro-physical characteristics of the donor–acceptor systems, on the other, constitutes a branch of the field under consideration whose development will permit the purposeful synthesis of donor–acceptor systems in the future.

The possibility of refining relations of the type $\delta = f(I_D - EA)$ depends in the first place on the accuracy of the determination of I_D and EA. Only the ionisation potential can be determined with adequate accuracy at the present time but usually this applies only to the vertical and not the

Table 2. The degree of charge transfer in π–π complexes and radical-ion salts.

No.	Donor	I_D, eV	Acceptor	δ	Conditions	Method	Refs.
1	Toluene	8.72	TCNQD	0.01	I	IRS	[57]
2	*o*-Xylene	8.6	"	0.02	I	"	[57]
3	Anisole	8.42	"	0.06	I	"	[57]
4	Naphthalene	8.12	"	0.08	II	"	[57]
	"	8.12	"	0.13	III	XDA	[77]
5	2-Ethylnaphthalene	8.0	"	0.06	I	IRS	[57]
6	Veratrol	7.99	"	0.08	I	"	[57]
7	Hexamethylbenzene	7.95	"	0.08	III	EAS	[74]
8	2,6-Dimethylnaphthalene	7.82	"	0.06	II	IRS	[58]
9	1-Methoxynaphthalene	7.72	"	0.15	I	"	[57]
10	Acenaphthene	7.66	"	0.05	III	EAS	[74]
11	Pyrene	7.53	"	0.05	III	"	[74]
12	Carbazole	7.6	"	0.12	III	"	[74]
13	*p*-Terphenyl	—	"	0.16	III	XDA	[77]
14	Anthracene	7.40	"	0.105	III	EAS	[74]
15	Perylene	7.12	"	0.15	III	XDA	[85]
16	Phenothiazine	7.14	"	0.2	III	"	[74]
17	Dimethyldihydrophenazine	6.9	"	0.3	III	"	[77]
18	*N*-Methylphenazine	6.8	"	0.63	III	RS	[86]
	"	6.8	"	0.63	III	IRS	[60]
	"	6.8	"	0.7	III	RRS	[87]
19	Tetramethyl-*p*-phenylenediamine	6.75	"	0.9	III	XDA	[88–90]
20	Tetrathiafulvalene	6.5	"	0.59	III	XES	[88–90]
	"	6.5	"	0.59	III	IRS	[60]
	"	6.5	"	0.56	III	XES	[33]
	"	6.5	"	0.59	III	ENS	[75]
	"	6.5	"	0.62	III	"	[75]
	"	6.5	"	0.61	IV	XDA	[77]
21	Tetramethyltetrathiafulvalene	6.3	"	0.72	III	XES	[91]
	"	6.3	"	0.63	III	IRS	[60]
22	Hexamethylenetetrathiafulvalene	6.3	"	0.72	III	"	[60]
23	Tetramethyltetraselenafulvalene	6.58	"	0.57	III	"	[60]
	"	6.58	"	0.21	III	—	[60]
24	Tetraselenafulvalene	7.17	"	0.63	III	IRS	[60]
25	Hexamethylenetetraselenafulvalene	6.6	"	0.74	III	"	[60]
26	Dibenzotetrathiafulvalene	6.8	"	0.46	III	"	[60]
27	Diphenyltetrathiafulvalene	6.55	"	0.46	III	"	[60]
28	Dimethyltetrathiafulvalene	6.3	"	0.68	III	"	[60]
29	Hexamethylenediselenadithiafulvalene	6.45	"	0.72	III	"	[60]
30	Tetrathiafulvalene	6.5	TFTCNQD	1.0	III	"	[60]
31	Dibenzotetrathiafulvalene	6.8	"	1.0	III	"	[60]
32	Hexamethylenetetrathiafulvalene	6.3	"	1.0	III	"	[60]
33	Hexamethylenetetraselenafulvalene	6.6	"	1.0	III	"	[60]
34	Hydroquinone	7.95	BQ	0.21	III	XDA	[92]
35	Durene	8.3	CA	0.04	II	DM	[14]
	"	8.3	"	0.06	II	EAS	[14]
36	Naphthalene	8.12	"	0.04	II	DM	[14]
	"	8.12	"	0.02	II	EAS	[14]
37	Hexamethylbenzene	7.95	"	0.04	—	DM	[14]
	"	7.95	"	0.04	II	EAS	[14]
38	Pyrene	7.53	"	0.06	II	"	[14]
39	Anthracene	7.4	"	0.02	II	"	[14]
40	Tetrathiafulvalene	6.5	"	0.2	III	IRS	[93]
	"	6.5	"	0.27	III	XES	[93]
41	Durene	8.3	TNB	0.02	II	DM	[14]
	"	8.3	"	0.02	II	EAS	[14]
42	Naphthalene	8.12	"	0.03	II	DM	[14]
	"	8.12	"	0.02	II	EAS	[14]
43	Hexamethylbenzene	7.95	"	0.04	II	DM	[14]
	"	7.95	"	0.03	II	EAS	[14]
44	Durene	8.3	TCNE	0.06	II	DM	[14]
45	Hexamethylbenzene	7.95	"	0.07	II	"	[14]
	"	7.95	"	0.08	III	EAS	[73]
46	Naphthalene	8.12	"	0.06	III	DM	[14]
47	Acenaphthene	7.66	"	0.12	III	EAS	[73]
48	Dibenzofuran	7.9	"	0.05	III	"	[73]
49	Tetrathiafulvalene	6.5	3,3,5,5-tetrachloro-*p*-diphenoquinone	0.81	III	XES	[93]
50	"	6.5	3,3,5,5-tetrabromo-*p*-diphenoquinone	0.36	III	"	[93]
51	"	6.5	pyromellitic dianhydride	0.54	III	"	[93]
52	"	6.5	2,3-dichloro-5,6-dicyano-1,4-benzoquinone	1.0	III	"	[93]
53	Tetramethyltetratetrathiafulvalene	6.3	TCNE	0.96	II	IRS	[63]

Notation. IRS = Infrared spectroscopy, RS = Raman spectroscopy, RRS = resonance Raman spectroscopy, XES = X-ray electronic spectroscopy, ENS = elastic neutron scattering, and DM = determination of dipole moments; TFTCNQD = tetrafluoro-7,7,8,8-tetracyanoquinodimethane. Conditions in the measurements: I) solution of the donor; II) solution; III) crystalline state; IV) crystalline state at a pressure of 4.6 kbar.

adiabatic ionisation potentials, which would have to be used in the analysis of rules governing the variation of δ. The latest studies in this field have shown[101] that only in the case of aromatic hydrocarbons is the discrepancy between the vertical and adiabatic ionisation potentials small ($\leqslant$0.1 eV). On the other hand, in the case of donors such as tetrathiafulvalenes the discrepancy is considerable (from 0.35 to 0.52 depending on the substituents). As regards electron affinity, the accuracy of its determination is undoubtedly inferior to that of the determination of I_D, which, together with the errors in the determination of the values of δ, can lead to an additional distortion of the experimental relation.

Taking into account the factors above, the experimental relation (Fig.5) must be regarded as very satisfactory. One should also note that, in determining this relation, no account was taken of the structural characteristics of the donor and the acceptor which could alter quantities such as both S_{01} and E_C and E_M. It may be that some information about the changes in E_C and E_M is contained in an implicit form in characteristics of the donor and acceptor such as the half-wave potential for the anodic oxidation ($E^{ox}_{1/2}$) and the half-wave potential for the polarographic reduction ($E^{red}_{1/2}$), because they contain information about the solvation energies (E_C and E_M depend on the ionic radius and the charge density). Since the quantities $E_{1/2}$ characterise in addition adiabatic processes, the determination of the correlation between δ and $E^{ox}_{1/2} - E^{red}_{1/2}$ is of undoubted interest.

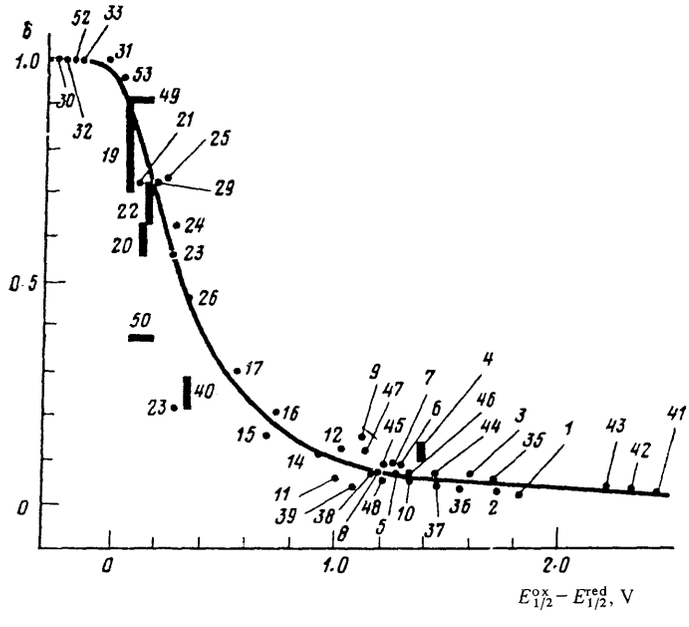


Figure 6. Dependence of the experimental values of δ on the difference $E^{ox}_{1/2} - E^{red}_{1/2}$. Ther electrochemical characteristics of the components were taken from Refs.10, 98, and 102–104; the numbering of the points corresponds to the numbering of the complexes in Table 2.

It follows from Fig.6 that such a correlation does obtain and that in the region of high degrees of CT it is more pronounced than the relation between δ and $I_D - EA$. With its aid, it is possible to predict fairly accurately the degree of CT solely from two characteristics of the donor and acceptor which can be comparatively readily determined, namely $E^{ox}_{1/2}$ and $E^{red}_{1/2}$.

It is noteworthy that some scatter in the experimental points is nevertheeless observed. This may indicate the need to take into account also more refined characteristics of the donor–acceptor system, for example, the changes in overlap integrals, etc.

V. CONCLUSION

The synthesis and investigation of organic complexes and radical-ions with unusual electrophysical characteristics have developed vigorously in recent times. Theoretical ideas permitting the choice of the initial components of the complex for the synthesis of systems having particular properties with a definite reliability have therefore assumed special importance. We believe that the road to these theoretical ideas leads via the determination of a relation between characteristics of the components such as the ionisation potential (the anodic oxidation half-wave potential) and electron affinity (the polarographic reduction half-wave potential) and a characteristic of the complex such as the degree of charge transfer. Here many theoretical and practical problems remain, although the relations obtained already permit a purposeful selection of the components of the complex at a specific level. There is no doubt that, as more accurate methods for the determination of the degree of charge transfer develop and as more extensive experimental data accumulate, relations of the property of the component–property of the complex type will be to a considerable degree refined.

REFERENCES

1. S.I.Peredereeva, I.G.Orlov, and M.N.Cherkashin, Uspekhi Khim., 1975, **44**, 602 [Russ.Chem.Rev., 1975(4)].
2. F.Gutmann and L.E.Lyons, "Organic Semiconductors" (Translated into Russian), Izd.Mir, Moscow, 1970, p.696.
3. A.D.Grishina and A.V.Vannikov, Uspekhi Khim., 1979, **48**, 1393 [Russ.Chem.Rev., 1979(8)].
4. E.B.Yagubskii and M.L.Khidekel', Uspekhi Khim., 1972, **41**, 2132 [Russ.Chem.Rev., 1972(12)].
5. H.J.Keller (Editor), "Chemistry and Physics of One-Dimensional Metals", Plenum Press, New York, 1977, p.426.
6. A.A.Ovchinnikov and V.Ya.Krivnov, Izv.Akad.Nauk Latv.SSR, Ser.Fiz.i Tekh.Nauk, 1981, (6), 55.
7. O.Neilands, Izv.Akad.Nauk Latv.SSR, Ser.Fiz.i Tekh.Nauk, 1981, (6), 63.
8. V.N.Laukhin and I.F.Shchegolev, Izv.Akad.Nauk Latv.SSR, Ser.Fiz.i Tekh.Nauk, 1981, (6), 78.
9. A.N.Aleksandrov, A.Karutz, I.V.Krivoshei, T.B.Litinskii, V.E.Starov, V.E.Umanskii, and Fan Yayong, "Elektronnoe Stroenie Kvaziodnomernykh Organicheskikh Metallov" (The Electronic Structure of Quasi-One-Dimensional Organic Metals), Vol.1, "Problema Vybora Struktury" (The Problem of the Selection of Structure), Preprint, Fiziko-Tekhnicheskii Institut Akad.Nauk Ukrain.SSR, Kharkov, 1975, p.56.
10. G.Sato and J.P.Ferraris, Bull.Chem.Soc.Japan, 1980, **53**, 2141.
11. Z.G.Soos, J.Chem.Educ., 1978, **55**, 546.

12. M.L.Khidekel' and E.I.Zhilyaeva, Zhur.Vses.Khim. Obshch.im.Mendeleeva, 1978, **23**, 506.
13. R.S.Wheland and J.L.Gillson, J.Amer.Chem.Soc., 1976, **98**, 3917.
14. G.Briegleb, "Elektron-Donator-Acceptor Complexe", Springer Verlag, Berlin, 1961, p.279.
15. R.S.Mulliken and W.B.Person, "Molecular Complexes", Acad.Press, New York, 1969, p.498.
16. E.N.Gur'yanova, I.P.Gol'dshtein, and I.P.Romm, "Donorno-Aktseptornaya Svyaz'" (The Donor–Acceptor Bond), Izd.Khimiya, Moscow, 1973, p.397.
17. R.Foster (Editor), "Molecular Complexes", Elec.Sci., London, 1973, Vol.1, p.369.
18. R.Foster (Editor), "Molecular Complexes", Elec.Sci., London, 1974, Vol.2, p.305.
19. R.Foster, "Organic Charge Transfer Complexes", Acad.Press, New York, 1969, p.470.
20. O.Kh.Poleshchuk and Yu.K.Maksyutin, Uspekhi Khim., 1976, **45**, 2097 [Russ.Chem.Rev., 1976(12)].
21. V.Kampar and Z.Bruvers, Zhur.Obshch.Khim., 1981, **51**, 2331.
22. V.Kampar, Z.Bruvers, and R.Kampare, "Tezisy Dokladov V Vsesoyuznogo Soveshchaniya po KPZ i Ion-Radikal'nym Solyam" (Abstracts of Reports at the Vth All-Union Conference on Charge-Transfer Complexes and Radical-Ion Salts), Inst.Khim.Fiz. Akad.Nauk SSSR, Chernogolovka, 1981, p.43.
23. J.Sauer and H.Mushorph, Adv.Mol.Relax.Proc., 1976, **8**, 177.
24. A.Z.Dzhumanazarova, I.A.Abronin, V.P.Litvinov, G.M.Zhidomirov, and V.A.Korsunov, Khim. Geterotsikl.Soed., 1979, 1456.
25. T.Ohta, H.Kuroda, and T.L.Kunii, Theor.Chim. Acta, 1970, **19**, 167.
26. Z.Yoshida and I.Kobayashi, Theor.Chim.Acta, 1971, **23**, 67.
27. O.Kysel, Z.phys.Chem., 1974, **89**, 62.
28. T.Ohta, T.Tujikawa, and H.Kuroda, Bull.Chem.Soc. Japan, 1974, **47**, 2115.
29. K.Yakushi, M.Iguchi, and H.Kuroda, Bull.Chem. Soc.Japan, 1979, **52**, 3180.
30. R.J.W.Le Fevre, D.V.Radford, and D.J.Stiles, J. Chem.Soc., B, 1968, 1297.
31. A.Weiss, Adv.Nucl.Quadr.Res., 1974, 1, 1.
32. Yu.K.Makosytin, T.A.Babushkina, E.N.Guryanova, and G.K.Semin, Theor.Chim.Acta, 1969, **14**, 48.
33. I.Ikemcto, M.Yamada, T.Sugano, and H.Kuroda, Bull.Chem., Soc.Japan, 1980, **53**, 1871.
34. Y.Matsunaga, Bull.Chem., Soc.Japan, 1969, **42**, 2170.
35. Y.M.Issa, A.E.El Khol, A.M.Hindawey, and R.M.Issa, J.Indian Chem.Soc., 1980, **57**, 216.
36. J.Koziol and P.Tomasik, Bull.Acad.Polon.Sci., Ser. Sci.Chim., 1979, **27**, 335.
37. A.M.Hindawey, A.M.G.Nassar, and R.M.Issa, Acta Chim.Acad.Sci.Hung., 1977, **92**, 263.
38. Y.Matsunaga, J.Chem.Phys., 1964, **41**, 1609.
39. R.M.Issa and M.M.El'Essawey, Z.phys.Chem., 1973, **253**, 96.
40. G.Varsayi and M.Kubinyi, J.Mol.Struct., 1978, **45**, 107.
41. I.Yarwood, in "Spectroscopy and Structure of Molecular Complexes", Plenum Press, London, 1973, p.105.
42. B.Moszynska and A.Tramer, J.Chem.Phys., 1967, **46**, 820.
43. B.Hall and J.P.Devlin, J.Phys.Chem., 1967, **71**, 465.
44. B.Moszynska, Acta Phys.Polon., 1968, **33**, 959.
45. M.Saheki and H.Yamada, Spectrochim.Acta, 1976, **32A**, 1425.
46. H.B.Friedrich and W.B.Person, Chem.Phys., 1966, **44**, 216.
47. A.Suharda-Sobzyk, L.Syper, and L.Sobczyk, J. Chem.Soc., Faraday Trans.II, 1975, 1994.
48. J.P.Larkindale and D.J.Simkin, J.Chem.Phys., 1972, **56**, 3730.
49. M.Rossi and E.Haselbach, Helv.Chim.Acta, 1979, **62**, 140.
50. M.A.Slifkin, Spectrochim.Acta, 1973, **29A**, 835.
51. W.Pietrzycki, Roczn.Chem., 1976, **50**, 1555.
52. P.W.Jensen, Chem.Phys.Letters, 1977, **45**, 415.
53. K.H.Michaelian, K.E.Rieckhoff, and E.M.Voight, Chem.Phys.Letters, 1973, **23**, 5.
54. M.Ohmasa, M.Kinoshita, and H.Akamatu, Bull. Chem.Soc.Japan, 1971, **44**, 3296.
55. H.Yamada and M.Kawamori, Spectrochim.Acta, 1971, **27A**, 2425.
56. J.P.Larkindale and D.J.Simkin, Spectrochim.Acta, 1972, **28A**, 485.
57. V.Kampar, S.Valtere, and O.Neilands, Teor.Eksper. Khim., 1978, **14**, 369.
58. V.Kampar, I.Gudele, and O.Neilands, Teor.Eksper. Khim., 1980, **16**, 415.
59. V.Kampar, I.Gudele, R.Kampare, S.Valtere, and O.Neilands, Zhur.Obshch.Khim., 1981, **51**, 2553.
60. J.C.Chapell, A.N.Bloch, W.A.Bryden, M.Maxfield, T.O.Pochler, and D.O.Cowan, J.Amer.Chem.Soc., 1981, **103**, 2442.
61. M.A.Slifkin, Chem.Phys.Letters, 1970, **7**, 195.
62. B.Moszynska-Mierzecka, Acta Phys.Polon., 1977, **52A**, 355.
63. V.Kampar, Izv.Akad.Nauk Latv.SSR, Ser.Khim., 1982, (3), 283.
64. A.Girlando and C.Pecile, J.Mol.Spectr., 1979, **77**, 374.
65. B.R.Clark and D.H.Evans, J.Electroanal.Chem., 1976, **69**, 181.
66. Y.Iida, Bull.Chem.Soc.Japan, 1977, **50**, 1337.
67. Y.Iida, Bull.Chem.Soc.Japan, 1974, **47**, 99.
68. A.Girlando, I.Zanon, R.Bozio, and C.Pecile, J. Chem.Phys., 1978, **68**, 22.
69. R.Bozio, A.Girlando, and C.Pecile, Chem.Phys., 1977, **21**, 257.
70. T.J.Kistenmacher, J.L.de Boer, and A.Vos, Acta Cryst., 1977, **B33**, 602.
71. V.Van Bodegom, J.L.De Boer, and A.Vos, Acta Cryst., 1977, **B33**, 602.
72. P.Coppens and T.N.G.Row, Ann.New York Acad. Sci., 1978, **313**, 244.
73. M.Tanaka, Bull.Chem.Soc.Japan, 1977, **50**, 2881.
74. M.Tanaka, Bull.Chem.Soc.Japan, 1978, **51**, 1001.
75. J.Tanaka and M.Tanaka, Mol.Cryst.Liq.Cryst., 1979, **52**, 221.
76. A.N.Fedotov, I.P.Gol'dshtein, and E.N.Gur'yanova, "Tezisy Dokladov V Vsesoyuznogo Soveshchaniya po KPZ i Ion-Radikal'nym Solyam" (Abstracts of Reports at the Vth All-Union Conference on Charge-Transfer Complexes and Radical-Ion Salts), Inst.Khim.Fiz. Akad.Nauk SSSR, Chernogolovka, 1981, p.128.
77. P.S.Flandrois and D.Chasseau, Acta Crys., 1977, **B33**, 2744.
78. P.Coppens, Phys.Rev.Letters, 1975, **35**(2), 98.
79. S.Megtert, R.Comes, C.Vettier, R.Pynn, and A.F.Garito, Solid State Comm., 1979, **31**, 977.
80. Z.G.Soos, H.J.Keller, K.Ludolf, J.Queckborner, D.Wehe, and S.Flandrois, J.Chem.Phys., 1981, **74**, 5287.
81. H.M.McConnell, B.M.Hoffman, and R.M.Metzger, Proc.Nat.Acad.Sci.USA, 1965, **53**, 46.

82. P.L.Nordio and Z.G.Soos, J.Chem.Phys., 1970, **53**, 4077.
83. Z.G.Soos and D.J.Klein, Treatise Solid State Chem., 1976, **31**, 679.
84. V.Ya.Krivnov and A.A.Ovchinnikov, Fiz.Tverd.Tela, 1973, **15**, 172.
85. A.W.Hanson, Acta Cryst., 1978, **34B**, 2339.
86. H.Kuzmany and M.Elbert, Solid State Comm., 1980, **35**, 597.
87. Z.G.Soos, S.Mazumdar, and T.T.P.Cheunh, Mol. Cryst.Liq.Cryst., 1979, **52**, 93.
88. F.Denoyer, R.Comes, A.F.Garito, and A.J.Heeger, Phys.Rev.Letters, 1975, **35**, 445.
89. H.A.Mook and C.R.Watson, Phys.Rev.Letters, 1976, **36**, 801.
90. G.Shirane, S.M.Shapiro, R.Comes, A.F.Garito, and A.J.Heeger, Phys.Rev.Letters, 1976, **14**, 2325.
91. B.D.Silverman, J.Chem.Phys., 1978, **69**, 2585.
92. T.Sakurai, Acta Cryst., 1965, **19**, 320.
93. I.F.Golovkina, I.V.Krivoshei, V.A.Starodub, V.G.Aleshin, I.M.Gella, V.V.Nemoshkalenko, A.N.Senkevich, and Yu.N.Surov, Probably Teor. Eksper.Khim., 1979, **15**, 181.
94. N.Sato, K.Seki, and H.Inokuchi, J.Chem.Soc., Faraday Trans.II, 1981, **77**, 1621.
95. V.Kampar, D.Bite, L.F.Sukhodub, and O.Neilands, Zhur.Obshch.Khim., 1978, **48**, 663.
96. R.Gleiter, M.Koboyashi, J.Spanget-Larsen, J.P.Ferraris, A.N.Bloch, K.Bechgaard, and D.O.Cowan, Ber., 1975, **79**, 1218.
97. K.Bechgaard, D.O.Cowan, and A.N.Bloch, "The IVth International Symposium on the Organic Solid State" Bordeaux University (France), 1975, p.71.
98. V.Kampar and O.Neilands, Uspekhi Khim., 1977, **46**, 945 [Russ.Chem.Rev., 1977(6)].
99. I.B.Torrance "Mol.Metals.Proc.NATO Conf." New York–London, 1979, p.7.
100. T.J.Kistenmacher, T.J.Emge, F.M.Wiygul, W.A.Bryder, J.S.Chappell, J.P.Stockes, L.Y.Chiang, D.O.Cowan, and A.N.Bloch, Solid State Comm., 1981, **39**, 415.
101. N.Sato, K.Seki, and H.Inokuchi, J.Chem.Soc., Faraday Trans., II, 1981, **77**, 1621.
102. E.S.Pysh and N.C.Yang, J.Amer.Chem.Soc., 1963, **85**, 2124.
103. A.Zeig, W.G.Hodson, and W.H.Jura, J.Amer.Chem. Soc., 1964, **86**, 4124.
104. D.Parker, J.Amer.Chem.Soc., 1976, **98**, 98.

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