

# THE CONDITIONS FOR CHARGE TRANSFER IN ORGANIC SYSTEMS

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Organic polymers with conjugate bonds give narrow (4-8 oersted) single electron paramagnetic resonance (e.p.r.) signals of Lorentz form with a g-factor close to the pure spin value, the intensity of the signals increasing regularly with the length of the conjugate system and not changing when the polymer is dissolved [1-4]. The number of unpaired electrons  $N$  is  $10^{-5}$ - $10^{-1}$  of the number of macromolecules and is almost independent of temperature.

In crystals of low molecular weight compounds having conjugate bonds (polyacenes, hydrocarbons, their derivatives, dyes of various classes) a similar effect is found, but with the differences that the absorption disappears reversibly on solution and its intensity depends on the mode of crystallization [5-9]. For them  $N$  is  $2 \times 10^{-4}$ - $10^{-2}$  of the number of molecules and is also temperature independent. Two-component donor-acceptor crystals in which one of the components has a reduced ionization potential  $I$  and the other a positive electron affinity  $A$  have similar magnetic properties.  $N$  varies from  $4 \times 10^{-3}$  to 0.8 of the number of pairs and increases symbatically with a decrease in  $I-A$  [10,11]. Nevertheless, in all cases  $N$  is independent of temperature to  $4^\circ\text{K}$ .

Systems of all three types exhibit an increased electrical conductivity which obeys an exponential law [3, 12, 14]. In single-component crystals the activation energy of the dark conductance  $\varepsilon$  coincides with the threshold photoconductivity  $\varepsilon_\phi$  and the energy of the singlet-singlet transition [15]:

$$\varepsilon = \varepsilon_\phi = \varepsilon_0. \quad (1)$$

A study of photoconductivity shows that the photocurrent is not fundamental but depends on the thermal activation of carriers raised to local levels by the light [16, 23]. The connection between the carrier concentration and the number of unpaired electrons is not linear. In particular there are mixed crystals with equal concentrations of unpaired electrons, the conductivities of which differ by six orders of magnitude [14].

On the basis of the facts presented it can be stated that the appearance of unpaired electrons and current carriers in the compounds in question is connected with local conditions.\* A characteristic property of systems with conjugate bonds is a low value of  $I-A$  and high electron polarizability; therefore the spectra of polar excitation (the condition for charge transfer) must be depressed compared with ordinary organic compounds. The necessity of taking into consideration the polar conditions in studies of the magnetic and electrical properties of molecular systems of this type were pointed out in [17]. In the present work the assumption is made that local conditions, determining the magnetic and electrical properties of compounds of these three types, are conditions involving the charge transfer either between molecules or between independent regions of unsaturation in a molecule. On the basis of this hypothesis it is possible to explain the formation of carriers by the dissociation of charge transfer complexes (c.t.c.), as first proposed by Lyons [18].

We examine the conditions for formation of local charge transfer structures in crystals, and their concentration. For this we consider the potential curves for complex formation between two molecules in neutral and polar states (Fig. 1). Since the dispersive interaction of systems of two ions is at least no less than that of neutral molecules, and in addition there is a strong coulombic interaction between ions, the equilibrium distance between components during the formation of c.t.c. must be less than between neutral molecules.

\*In order to explain the magnetic properties it could perhaps be assumed that intermolecular reaction in sufficiently long conjugated short chains leads to partial mixing of the ground state and lower excited magnetic states. However, a calculation carried out by D. A. Popov (Diploma work, Moscow State University, 1961) has shown that this mechanism does not apply for any length of conjugated system.

$$R_0^i < R^0. \quad (2)$$

This relationship (2) was recently confirmed experimentally [19]. The energy difference between the neutral and polar state is:

$$\epsilon_i^0 = I - A - W(R_0^i), \quad (3)$$

where  $W(R_0^i)$  is the coulombic interaction energy in the polar state. Equation (3) is also correct in the case of single-component crystals [17]. In solution the energy difference between the basic and polar states is

$$\epsilon_i^S = I - A - W(R_0^i) - W_S, \quad (4)$$

where  $W_S$  is the solvation energy in forming an ion pair. According to data in [20] the concentration of complexes,  $n$ , is related to the ion pair concentration in solution,  $N_0$ , by the relationship:

$$\frac{n^2}{N_0 - n} = N_0 e^{-\epsilon_i^S/kT}. \quad (5)$$

In the limit,  $N_0$  reaches a maximum, so that the number of polar states appearing in the crystal during its formation will be greater than in solution. In accordance with inequality (2) the appearance of polar states leads to local deformation of the crystal, whereupon

$$\epsilon_0(R_0^i) > \epsilon_l(R_0^i). \quad (6)$$

Thus, the local condition of c.t.c. in the crystal represents the growth of a dislocation in which the molecules are arranged at reduced distances from one another compared with the equilibrium distances in the neutral crystal. Naturally an analogous mechanism applies also for other methods of obtaining the solid. On the strength of (6), conversion from the polar to the neutral state is not possible without reorganization of a significant region in the crystal. The concentration of local c.t.c. is in addition independent of temperature and is determined by values of the ionization potentials and the electron affinity—as follows from (4) and (5). This model may be tested experimentally by a study of changes in the concentration of polar states on preparing crystals from solvents with different dielectric constants at different temperatures.

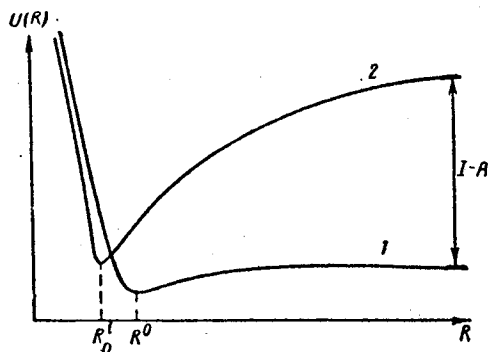


Fig. 1. Potential curves for neutral pairs (1) and for c.t.c. (2).

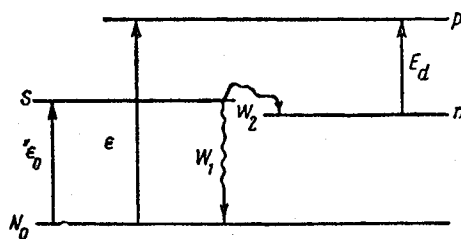


Fig. 2. Diagram of levels in an organic semiconductor. p) Conduction band; n) local level, specified as c.t.c.; S) singlet excited level.

Proceeding to the electrical conductivity of molecular crystals, it is necessary to determine the dissociation energy of the local charge transfer state to form a central ion, localized on the defect, and a free carrier. This amounts to the determination of the polarization energy of the crystal due to the c.t.c. and due to two infinitely remote molecular ions. The problem was solved by the methods of polar quantum theory. It was found that the motion of an electron current in the molecular crystal is accompanied by a wave of electronic polarization following

adiabatically after the electron. The latter leads to a decrease in the natural energy of the electron current. The polarization energy, in the crystal, of negative and positive molecular ions is approximately the same and is given by

$$E = -\frac{D}{v_0} K_{nn} \sum_i \frac{f_i}{\varepsilon_i^2}, \quad (7)$$

where  $D$  is a numerical coefficient determined by the crystal geometry;  $v_0$  is the molecular volume in the crystal;  $K_{nn}$  is the integral coulomb interaction of two electrons in the outer completed orbit of the molecule;  $f_i$  and  $\varepsilon_i$  are the oscillator strengths and excitation energies of the states. From (7) it is seen that with a decrease in the excitation energies the polarization energy increases quadratically.

|             | E, eV | E <sub>d</sub> , eV |
|-------------|-------|---------------------|
| Naphthalene | 1.08  | 1.47                |
| Anthracene  | 1.39  | 1.08                |
| Naphthacene | 1.76  | 0.78                |
| Pentacene   | 1.95  | 0.48                |

The results of calculations of polarization energies  $E$  and dissociation energies  $E_d$  for polar states in crystals of aromatic hydrocarbons are given in the table. Even for comparatively simple systems the polarization energy proved to be very large. An experimental value of the polarization energy, equal to the difference in ionization potentials in the gas and in the crystal, is known for anthracene and is  $1.59 \pm 0.25$  eV [18], which is close to the calculated value. It has been shown that dissociation of the charge transfer complex requires an expenditure of energy given by

$$E_d = -\left(1 - \frac{2D}{v_0} \sum_i \frac{f_i}{\varepsilon_i^2}\right) W(R'_i). \quad (8)$$

Values of  $E_d$  are given above.

The dissociation energies fall comparatively quickly with increasing geometrical molecular dimensions and with an increase in polarization.

In connection with the proposed model of local centers with charge transfer there arises an additional possibility for the appearance of current carriers in molecular crystals. This mechanism is based on the dissociation of c.t.c. owing to the energy of excitons. It has been found that the probability of exciton energy transfer to a local center of c.t.c. increases the probability of spontaneous emission of an exciton quantum if the concentration of local states exceeds  $10^{16} \text{ cm}^{-3}$ . Processes of this type are well known in organic semiconductors [21, 22].

An energy level diagram of the proposed model is given in Fig. 2. The photoconduction energy will coincide with the singlet-singlet transition energy. The stationary concentration of carriers  $p$  also will depend on the equilibrium exciton concentration and is determined from

$$p = N_0 e^{-\varepsilon_u/2kT} + n e^{-E_d/2kT} + \gamma \frac{N_0}{(1 + W_1/W_2)} e^{-\varepsilon_s/2kT}, \quad (9)$$

where  $W_1$  and  $W_2$  are the respective probabilities of deactivation and decomposition of the excitons, and  $\gamma \approx 1$ . With conduction bands located above the lower singlet level and at comparatively small concentrations of c.t.c.

$$\varepsilon_u > \varepsilon_0, \quad n e^{-E_d/2kT} < N_0 e^{-\varepsilon_s/2kT} \quad (10)$$

the carrier concentration will be determined by the energy of the singlet-singlet transition. If the conduction band is located below the excited singlet level, the principal source of carriers is in the conduction zone itself, as first reported in [9]. At high concentrations of c.t.c. the activation energy of electroconductivity coincides with the dissociation energy of the polar states, in conformity with (8) and (9).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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