PHYSICAL CHEMISTRY

V. A. BENDERSKII and L. A. BLUMENFELD

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. A. BENDERSKII and L. A. BLUMENFELD

CHARGE-TRANSFER STATES IN ORGANIC SYSTEMS

(Presented by Academician V. N. Kondrat' ev, January 8, 1962)

Organic polymers with conjugated bonds exhibit narrow single electron-paramagnetic-resonance (EPR) signals of Lorentzian shape, with a g-factor close to the purely spin value, whose intensity increases regularly with the length of the conjugated system and does not change upon dissolution ($^{1-4}$). The number of unpaired electrons N is 10^{-5}–10^{-1} of the number of macromolecules and is practically independent of temperature.

In crystals of low-molecular-weight compounds with conjugated bonds (polyacene hydrocarbons, their derivatives, dyes of various classes) an analogous effect is observed, with the difference, however, that the absorption reversibly disappears upon dissolution, and its intensity depends on the method of crystallization ($^{5-9}$). For them N is equal to 2×10^{-4}–10^{-2} of the number of molecules and likewise does not depend on temperature. Two-component donor-acceptor crystals, one of whose constituents has a lowered ionization potential I, and the other a positive electron affinity A, possess the same magnetic properties. N amounts from 4×10^{-3} to 0.8 of the number of pairs and increases symbatically with decreasing $I - A$ (^{10,11}). Nevertheless, in all cases N does not depend on temperature down to 4°K.

Systems of all three types possess enhanced electrical conductivity, obeying an exponential law (^{3,12,14}). For one-component crystals the activation energies of dark conductivity ε coincide with the photoconductivity threshold ε_ϕ and with the energy of the singlet-singlet transition (^{15}):

$$\varepsilon = \varepsilon_\phi = {}'\varepsilon_0. \tag{1}$$

The study of photoconductivity shows that the photocurrent is not primary, but is caused by thermal activation of carriers thrown by light onto local levels (^{16,23}). There is no direct connection between the carrier concentration and the number of unpaired electrons. In particular, there exist mixed crystals with the same concentration of unpaired electrons whose electrical conductivities differ by 6 orders of magnitude (^{14}).

Fig. 1. Potential curves for a neutral pair (1) and a CTC (2)

Figure 1: Fig. 1. Potential curves for a neutral pair (1) and a CTC (2)

On the basis of the facts set forth, it may be asserted that the appearance both of unpaired electrons and of current carriers in the compounds under consideration is connected with local states* . A characteristic property of systems with conjugated bonds is low values of $I - A$ and high electronic polarizabilities; therefore the spectrum of polar excitations (charge-transfer states) must be lowered in comparison with ordinary organic compounds. The necessity of taking polar states into account in studying the magnetic and electrical properties of molecular systems of this type was pointed out in (17). In the present work the supposition is advanced that the local states determining the magnetic and electrical— the chemical properties of compounds of these three types are states with charge transfer either between molecules or between individual conjugated segments in a molecule. On the basis of this hypothesis, one can explain the formation of carriers by dissociation of charge-transfer complexes (CTC), as was first proposed by Lyons (18).

Let us determine the conditions for the formation of local states with charge transfer in crystals and their concentration. To this end, let us consider the potential curves for the formation of a complex from two molecules in the neutral and polar states (Fig. 1). Since the dispersion interaction for a system of two ions is at least no smaller than for neutral molecules, and in addition a strong Coulomb interaction appears between ions, the equilibrium distance between the components upon formation of a CTC must be smaller than between neutral molecules.

Fig. 1. Potential curves for a neutral pair *(1)* and a CTC *(2)*

$$R_0^i < R^0. \tag{2}$$

Relation (2) has recently been confirmed experimentally (19). The energy difference between the neutral and polar states is equal to:

$$\varepsilon_i^0 = I - A - W(R_0^i), \tag{3}$$

---

* To explain the magnetic properties one might suppose that intermolecular interaction in sufficiently long conjugated chains leads to partial mixing of the ground and lower excited triplet state. However, calculation of charge levels carried out by D. A. Popov (diploma work, Moscow State University, 1961) showed that, for any length of the conjugated system, this mechanism does not occur.

where $W(R_i^0)$ is the energy of Coulomb interaction in the polar state. Relation (3) is also valid in the case of one-component crystals (^{17}). In solution the energy difference between the ground and polar states is equal to

$$\varepsilon_i^S = I - A - W(R_0^i) - W_S, \tag{4}$$

where W_S is the solvation energy of the ionic pair formed. According to (^{20}), the concentration of complexes n is related to the concentration of pairs in solution N_0 by the relation:

$$\frac{n^2}{N_0 - n} = N_0 e^{-\varepsilon_i^S/kT}. \tag{5}$$

At the growth boundary N_0 has a maximum, so that the number of polar states appearing in the crystal during its formation will be higher than in solution. In accordance with inequality (2), the appearance of polar states leads to a local deformation of the crystal, with

$$\varepsilon_0(R_0^i) > \varepsilon_i(R_0^i). \tag{6}$$

Thus, a local CTC state in a crystal is a growth dislocation in which the molecules are located at distances from one another shortened in comparison with the equilibrium distances for a neutral crystal. Naturally, an analogous mechanism is also valid for other methods of obtaining the solid phase. By virtue of condition (6), transition from the polar state to the neutral one is impossible without rearrangement of a significant region of the crystal. The concentration of local CTCs in this case does not depend on temperature and is determined by the values of the ionization potentials and electron affinities, as follows from (4) and (5). An experimental test of this model may be the study of changes in the concentration of polar states when crystals are obtained from solvents with different dielectric constants at different temperatures.

Turning to the electrical conductivity of molecular crystals, it is necessary to determine the dissociation energy of a local state with charge transfer with

with the formation of a central ion, localized at the defect, and a free carrier. This problem reduces to determining the polarization energy of the crystal due to charge-transfer states and due to two infinitely distant molecular ions. The problem was solved by methods of quantum field theory. It was found that the motion of a conduction electron in a molecular crystal is accompanied by a wave of electronic polarization, adiabatically following the electron. The latter leads to a lowering of the proper energy of the conduction electron. The polarization energies of a crystal by negative and positive molecular ions are approximately the same and equal to

Fig. 2. Level scheme of the organic semiconductor model. p —conduction band; n —local level caused by charge-transfer states; S —singlet exciton band

Figure 2: Fig. 2. Level scheme of the organic semiconductor model. p —conduction band; n —local level caused by charge-transfer states; S —singlet exciton band

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

where D is a numerical coefficient determined by the geometry of the crystal; v_0 is the volume per molecule in the crystal; K_{nn} is the Coulomb-interaction integral of two electrons on the highest filled orbital of the molecule; f_i, ε_i are the oscillator strengths and energies of the excited states. From (7) it is evident that, as the energies of the excited states decrease, the polarization energy increases quadratically.

Fig. 2. Level scheme of the organic semiconductor model. p —conduction band; n —local level caused by charge-transfer states; S —singlet exciton band.

The results of numerical calculations of the polarization energy E and the dissociation energy E_d of polar states in crystals of aromatic hydrocarbons are presented in Table 1.

Table 1

	E, eV	E_d, eV		E, eV	E_d, eV
Naphthalene	1.08	1.47	Naphthacene	1.76	0.78
Anthracene	1.39	1.08	Pentacene	1.95	0.48

Even for comparatively simple systems the polarization energies proved to be very large. The experimental value of the polarization energy, equal to the difference between the ionization potentials in the gas phase and in the crystal, is known for anthracene and is 1.59±0.25 eV ([18]), which is close to the calculated value. It was shown that dissociation of a charge-transfer complex requires an expenditure of energy equal to

$$E_d = -\left(1 - \frac{2D}{v_0} \sum_i \frac{f_i}{\varepsilon_i^2}\right) W(R_0^i). \tag{8}$$

The numerical values of E_d are given above.

The dissociation energies decrease rather rapidly with increasing geometrical dimensions of the molecules and with increasing polarization energy.

In connection with the proposed model of local charge-transfer centers, there arises an additional possibility for the appearance of current carriers in molecular crystals. This mechanism is based on the dissociation of charge-transfer states at the expense of exciton energy. It was found that the probability of the process of transfer of exciton energy to a local charge-transfer center exceeds the probability of spontaneous emission of an exciton quantum if the concentration of local states exceeds 10^{16} cm^{-3}. Processes of this type are well known in inorganic semiconductors ($^{21,\ 22}$).

The level scheme of the proposed model is given in Fig. 2. The photoconductivity energy will coincide with the energy of the singlet–singlet transition. The stationary concentration of carriers p will also depend on the equi-

equilibrium concentration of excitons, determined by

$$p = N_0 e^{-\varepsilon_u/2kT} + ne^{-E_d/2kT} + \gamma \frac{N_0}{(1 + W_1/W_2)} e^{-\varepsilon_0'/2kT}, \tag{9}$$

where W_1 and W_2 are, respectively, the probabilities of the processes of deactivation and decay of excitons, $\gamma \approx 1$. When the conduction band is located above the lower singlet level and at comparatively low concentrations of charge-transfer states,

$$\varepsilon_u > \varepsilon_0', \qquad ne^{-E_d/2kT} < N_0 e^{-\varepsilon_0'/2kT} \tag{10}$$

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 main source of carriers is direct excitation into the conduction band, described by the first term in (9). At high concentrations of charge-transfer states, the activation energy of electrical conductivity coincides with the dissociation energy of polar states, according to (8) and (9).

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
30 XII 1961

CITED LITERATURE

1. A. A. Berlin, L. A. Blumenfeld et al., Vysokomolek. soed., **1**, 1361 (1959).
2. A. V. Topchiev, M. A. Geiderikh et al., DAN, **128**, 312 (1959).
3. L. A. Blumenfeld, A. A. Berlin et al., Zhurn. strukturn. khim., **1**, 103 (1960).

4. B. I. Liogon' kii, L. S. Lyubchenko et al., Vysokomolek. soed., **2**, 1494 (1960).
5. Yu. Sh. Moshkovskii, DAN, **130**, 1277 (1960).
6. J. Matsunaga, Canad. J. Chem., **37**, 1003 (1959); **38**, 323 (1960).
7. F. P. Chernyakovskii, A. E. Kalmanson, L. A. Blumenfeld, Optika i spektroskopiya, **9**, 786 (1960).
8. D. J. E. Ingram, J. E. Bennett, J. Chem. Phys., **22**, 1136 (1954).
9. R. Neiman, D. Kivelson, J. Chem. Phys., **35**, 102 (1961).
10. D. Bijl, H. Keiner, A. C. Rose-Innes, J. Chem. Phys., **30**, 705 (1953).
11. J. Matsunaga, Bull. Chem. Soc. Japan, **29**, 582 (1956).
12. E. I. Balabanov, A. A. Berlin et al., DAN, **134**, 1123 (1960).
13. A. T. Vartanyan, Izv. AN SSSR, ser. fiz., **20**, 1541 (1956).
14. M. M. Labes, R. Sehr, M. Bose, J. Chem. Phys., **32**, 1570 (1960); **33**, 868 (1960).
15. A. T. Vartanyan, L. D. Rozenshtein, DAN, **131**, 273 (1960).
16. A. T. Vartanyan, ZhFKh, **20**, 1065 (1946).
17. L. A. Blumenfeld, V. A. Benderskii, DAN, **133**, 1451 (1960).
18. L. E. Lyons, J. Chem. Soc., 1957, 5001.
19. S. C. Wallwork, J. Chem. Soc., 1961, 494.
20. J. Czekalla, Zs. Elektrochem., **63**, 1157 (1959).
21. V. P. Zhuze, M. Ryvkin, Izv. AN SSSR, ser. fiz., **16**, 101 (1952).
22. L. Apker, E. Taff, Phys. Rev., **79**, 964 (1950); **81**, 698 (1951); **82**, 814 (1951).
23. H. Meier, Zs. phys. Chem., **206**, 340 (1958).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the *original.*