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J. Sworakowski [a]

[a] Department of Physical Chemistry, Institute of Organic and Physical Chemistry Worclaw Technical University, Wybrzeze Wyspiansiego 27, Wroclaw, Poland

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On the Origin of Trapping Centres in Organic Molecular Crystals

J. SWORAKOWSKI

Department of Physical Chemistry
Institute of Organic and Physical Chemistry
Wrocław Technical University
Wybrzeże Wyspianskiego 27, Wrocław, Poland

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Abstract—Traps for current carriers in molecular crystals may be due either to imperfections of the crystal structure (structural traps) or to chemical impurities introduced into the lattice (chemical traps). In the present paper simple hypotheses are presented explaining the formation of traps of the two groups. Perturbations of the crystal structure are not localized in one unit cell, but may extend over several farther cells. The local values of the polarization energy of the crystal lattice will change near to the centre of the defect, thus the " perturbed " molecules can act as traps for current carriers. Energetic distributions of traps as calculated under such conditions are found to be in a good agreement with those determined experimentally. Trapping states may be also formed by impurity molecules having either greater electron affinity or smaller ionization energy than the host ones. The depth of the chemical traps estimated from the relationships given in the paper has been compared with the experimental data.

1. Introduction

There are two main questions concerning the influence of trapping centres on the transport of current carriers in organic crystals: (i) what is their distribution and density, and (ii) what is their origin and nature. Measurements of steady-state space-charge-limited currents in single crystals and polycrystalline samples of naphthalene,(1) anthracene,(2–6) tetracene,(7) perylene,(8) *p*-terphenyl and *p*-quaterphenyl,(9–11) phthalocyanines(12–14) as well as in inorganic crystals have shown that the current is controlled by traps distributed in the forbidden gap. The energetic distribution has been approximated by the equation

$$h(E) = \frac{H}{kT_c} \exp\left(\frac{E}{kT_c}\right), \tag{1}$$

where $h(E)$ is the density of traps in the energy interval $(E, E + \mathrm{d}E)$,† H is the total trap density and kT_c is the characteristic energy of distribution. The total trap densities calculated from experimental data have usually been found to be 10^{16}–10^{19} cm^{-3}, their characteristic energies of distribution varying from 0.10 to 0.25 eV. As it was indicated,(16,17,14) the trap band consists of several discrete levels. Such trapping states were attributed to perturbations of the crystal structure.(16,18) Moreover, traps due to the presence of chemical impurities may occur in the crystals (see, for example, Ref. (19)). In the present paper the nature of such " structural " and " chemical " traps will be discussed.

It is known that simple molecular solids have the forbidden gap 2–6 eV wide, so that without making a great error one may consider them as free of thermally generated current carriers. The carriers have sufficiently low mobility to assume them to be successively localized on adjacent sites in the crystal. Furthermore, in the subsequent sections of this paper effects due to the crystal anisotropy will be neglected.

2. Structural Traps

As it has been first suggested by Lyons,(20) bands for excess free carriers may occur in molecular crystals, the positions of their edges with respect to the zero level (vacuum level) being established by the relations

$$E_v = -I_c; \quad E_c = -A_c. \tag{2}$$

Here E_v and E_c are the energies of the edges of the valence and conduction bands, respectively, and I_c and A_c denote the ionization energy and the electron affinity of a molecule in the crystal. Generally, the last two parameters are related to those of isolated molecules by the equations

$$I_c = I_g - P; \quad A_c = A_g + P, \tag{3}$$

where P is the polarization energy due to the introduction of the unit electric charge into the crystal. Lyons(20,21) has shown that the

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† As the zero point of the energy scale the edge of the conducting band has been chosen. In the forbidden gap $E < 0$, according to the convention accepted in this paper (cf. Ref. (5)).

polarization energy can be evaluated with a very good accuracy as the sum of the ion–dipole and dipole–dipole interactions

$$P = \sum_{i=1}^{n} \frac{\alpha e^2}{r_i{}^4} - \sum_{i<j} \alpha^2 e^2 r_i^{-3} r_j^{-3} d^{-3} \left\{ (\vec{r_i} \cdot \vec{r_j}) - 3d^{-2} (\vec{r_i} \cdot \vec{d}) (\vec{r_j} \cdot \vec{d}) \right\} \tag{4}$$

where α is the polarizability of the molecule, r_i and r_j are the distances of ith and jth molecules from the ion, and d is the distance between ith and jth molecules. The sum must be taken over all molecules in the crystal and all pairs of dipoles.

It can be shown that the contribution of the nearest neighbours to the energy of ion–dipole interaction amounts approximately to 70–80% and is almost independent of the presence of structure perturbations. The contribution of the dipole–dipole interactions is about 20% of total value of polarization energy and depends only slightly on imperfections in the crystal. Therefore in the semi-quantitative considerations the simplified model can be used, where one takes into account the interactions of the ions with its next-nearest neighbours, neglecting both interactions of the ion with farther molecules and all the dipole–dipole term; thus one obtains approximately

$$P = \beta r^{-4}, \tag{5}$$

where β is a constant and r is the distance.

Polarization energy is, of course, the same regardless of the position of the ionized molecule in an ideal crystal. In the real case, however, perturbations of the periodicity of the crystal lattice (dislocation, point defects) may cause local changes in the energy. Let us assume that in one point such a defect has changed the distance between adjacent molecules from its equilibrium value (r_0) to r_s. The perturbation is not localized in one unit cell only, but extends over several farther neighbouring cells. The action of repulsive and attractive van der Waals-type forces causes perturbation to diminish with the distance from the centre of the defect. The exact solution of this problem may be obtained only by complicated numerical calculations; to the first approximation, however, it seems reasonable to assume after Kitaigorodskii(22) that the magnitude of the perturbation changes according to the equation

$$r - r_0 = (r_s - r_0) \exp(-R/\rho) \tag{6}$$

where R is the distance from the centre of the defect and ρ is a constant. If $r < r_0$, the local value of the polarization energy will be greater than that in an ideal crystal; in other words the ionization energy of a molecule near to the defect is smaller and its electron affinity is greater, thus it may act as a trapping centre for current carriers with the depth equal to the difference of polarization energies. From Eqs. (5) and (6) one obtains

$$\Delta P = \beta(r^{-4} - r_0^{-4}) = \beta\{[r_0 + (r_s - r_0)\exp(-R/\rho)]^{-4} - r_0^{-4}\}, \qquad (7)$$

or, inserting the equation (5)

$$E = P_0\left\{1 - \left[1 + \frac{(P_0 - E_m)^{-1/4} - P_0^{-1/4}}{P_0^{-1/4}}\exp\left(-\frac{R}{\rho}\right)\right]^{-4}\right\} \qquad (8)$$

Here E_m is the energy of deepest traps, i.e. the change of the polarization energy in the centre of the defect ($E_m = P_0 - P_s$). As it may be seen, the function is roughly independent of the value of P_0.

It should be noted that the number of trapping centres associated with one dislocation is smaller than the number of dislocated molecules. Under steady-state conditions a first carrier approaching to the disordered region will be trapped in the deepest trap, i.e. in the centre of dislocation. Coulombic forces should prevent a subsequent carrier being trapped by any molecule at a distance closer than some distance R_c. The value is expected to be of order of several tens of angstroems, i.e. several intermolecular distances. The behaviour of the disordered region depends on the value of the quotient R_c/ρ. If $R_c > \rho$, only the centres of dislocation can act as trapping states; if $R_c < \rho$, the set of dislocations will behave as a quasicontinuous trap band with the lower edge at E_m. When R_c and ρ are both of the same order, one or two deepest levels possible to be filled will be well removed from the shallower quasicontinuous band beginning at an energy E_l. Since the number of molecules displaced in the same degree from their equilibrium positions is a power function of the distance from the centre of perturbation (it is proportional to the square of the distance in an isotropic three-dimensional sample), from the Eq. (8) the relationship describing the energetic distribution of traps in quasicontinuous band can be derived

$$h(E) = \chi \ln^2\left[\frac{P_0^{-1/4} - (P_0 - E_m)^{-1/4}}{P_0^{-1/4} - (P_0 - E)^{-1/4}}\right], \qquad (9)$$

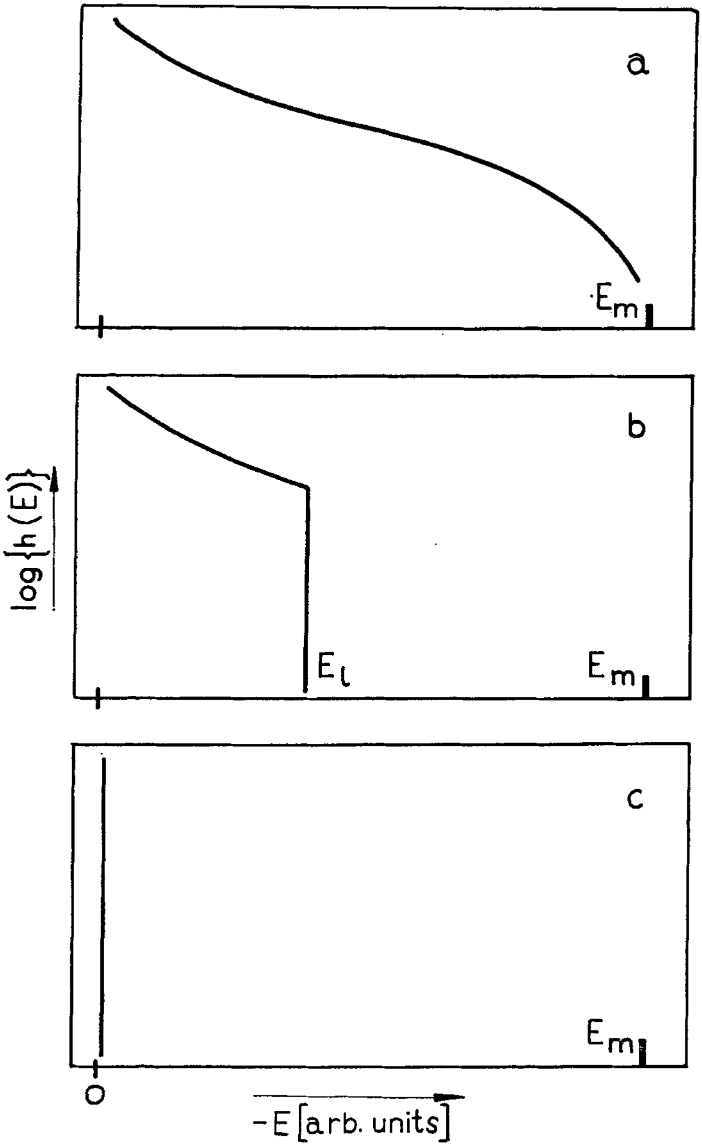

Figure 1. Trap distributions calculated for several assumed values or R_c/ρ: (a) $R_c/\rho = 0.1$, (b) $R_c/\rho = 1$, (c) $R_c/\rho = 10$.

Here χ denotes a parameter dependent on the trap density. In Figs. 1 and 2 trap distributions evaluated from Eq. (9) for several values of R_c/ρ and E_m are plotted against E. The function given by the Eq. (9) may be well approximated by the usual exponential distribution function (Eq. (1)) within a large energy range.

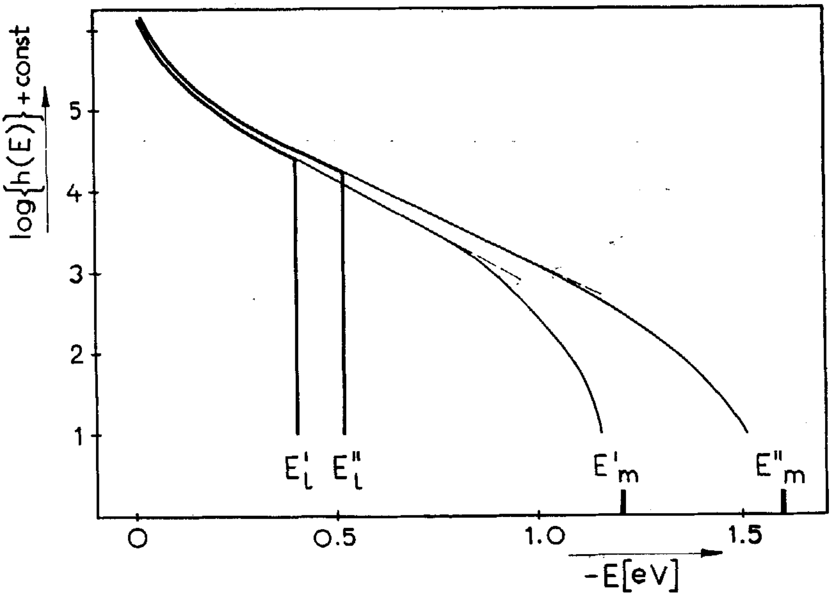

Figure 2. Trap distributions for $E_m = -1.2$ eV and $E_m = -1.5$ eV. Both curves are calculated assuming $R_c/\rho = 1$, $P_0 = 1.5$ eV. Thin solid lines show the function $h(E)$ as calculated from Eq. (9), thick ones correspond to the density of states possible to be filled. Dashed lines show the approximations by the exponential function (Eq. (1)). The distribution functions calculated from the Eq. (1) amount to 0.18 and 0.15 eV for upper and lower curves, respectively.

3. Chemical Traps

As it was stated before, trapping centres may be formed in the crystal by guest molecules having the ionization energies smaller or the electron affinities greater than the host ones.

The influence of impurities on the transport of current carriers has so far been studied on anthracene doped with tetracene, anthraquinone and—qualitatively—with perylene. The pioneer work of

Hoesterey and Letson(19) followed by other authors(23–25) have shown that tetracene molecules in anthracene crystal form shallow traps both for electrons and for holes. Anthraquinone does not form effective traps for holes, its molecules, however, act as traps for electrons.(19–26)

The investigations of the influence of impurities would be more effective if it was possible to predict the depth of traps formed by guest molecules (denoted next as " D ") in the crystal formed by host ones (denoted as " C "). A first approach to this problem has been proposed by Gutmann and Lyons.(27) According to the authors, the depth of electron and hole traps formed by guest molecules can be estimated as a difference of electron affinities or ionization potentials of isolated host and guest molecules, respectively. In this section of the paper a further attempt is given, where the influence of the crystal lattice is taken into consideration.

One may evaluate the depth of the hole traps from the equation

$$E_t^p = I_c^D - I_c^c, \tag{10}$$

where I_c^c and I_c^D are the ionization potentials of molecules C and D in the crystal lattice C, respectively. Similarly the depth of electron traps can be calculated as follows

$$E_t^n = A_c^c - A_c^D, \tag{11}$$

where A_c^c and A_c^D stand for the electron affinities of molecules C and D in the crystal C, respectively.

Similarly as in one-component crystals the ionization energies and electron affinities of molecules C and D in the crystal C are related to the gas-phase energies by the equations

$$\begin{aligned} A_c^c &= A_g^c + P \quad ; \quad & I_c^c &= I_g^c - P \\ A_c^D &= A_g^D + P' \quad ; \quad & I_c^D &= I_g^D - P' \end{aligned} \tag{12}$$

Here P and P' are the polarization energies due to the introduction of electric charge on the molecules C and D, respectively. Usually P' and P (in the vicinity of the impurity molecule) are somewhat greater than corresponding values in pure crystals C and D(28); moreover, $P' \neq P$ because of different interactions of environment with the molecules C and D. An exact calculation of the values of P and P' might be obtained only by complicated numerical computations. In semi-qualitative considerations presented here it seems reasonable, however, to assume that the value of P is equal to the polarization energy of molecule C in an undoped crystal, and the value of P' is close either to the polarization energy of molecule C in the crystal C or to the polarization energy of molecule D in crystal D. From Eqs. (10) to (12) after simple transformations one obtains

$$\begin{aligned} & I_g^D - I_g^c > E_t^p > I_D^D - I_c^c, \\ \text{or} \quad & \\ & I_g^D - I_g^c < E_t^p < I_D^D - I_c^c, \end{aligned} \tag{13}$$

and

$$\begin{aligned} & A_g^c - A_g^D > E_t^n > A_c^c - A_D^D, \\ \text{or} \quad & \\ & A_g^c - A_g^D < E_t^n < A_c^c - A_D^D, \end{aligned} \tag{14}$$

When the dimensions of guest molecules differ from those of the host ones, the introduction of impurity causes perturbations of the periodicity in the crystal lattice and in consequence structural traps, in addition to chemical ones, will occur in the crystal. According to the model presented in the previous section of the paper, their distribution parameters will depend on the magnitude of the perturbation due to the introduction of impurity molecules.

The validity of the model presented here can be proved by the comparison with experimental results. This was made in Table 1.

4. Conclusions

Despite of the considerable simplifications introduced, the parameters of the trap distribution and the depth of traps as predicted from equations given in this paper are in a quite good agreement with the experimental results. The trap distribution calculated from the Eq. (9) for several reasonable values of E_m may be well approximated by the exponential function.

The assumed model predicts for the parameters R_c and ρ being both of the same order a deep monoenergetic trapping level (or levels) and shallower trap band to occur in the crystal. This is quite similar to the assumption of Adolph,(33,34) based on observations of the time dependence of space-charge-limited currents in anthracene. Moreover, it follows from the model that the structural defects should form identical traps both for holes and electrons. This was confirmed by results obtained for anthracene(3–6) and tetracene.(7)

TABLE 1 The Depths of Traps Formed by Tetracene and Anthraquinone in Anthracene Crystals. All energies are given in electronvolts. For anthracene $I_c^c = 5.65$ eV,(28,30) $I_g^c = 7.38$ eV,(29) $A_c^c = 1.95$ eV,† $A_g^c = 0.74$ eV.‡

Impurity	I_D^D	I_g^D	A_D^D	A_g^D	$I_D^D - I_c^c$	E_t^p $I_g^D - I_g^c$	Exper.	$A_c^c - A_D^D$	E_t^n $A_g^c - A_g^D$	Exper.
Tetracene	5.25(28,30)	6.88(29)	2.15§	1.13‡	−0.40	−0.50	−0.41 Ref. 19 and 23–25	−0.20	−0.39	−0.17 Ref. 24
Anthraquinone	—	9.34(29)	—	1.28‡	—	$E > 0$	Does not form traps	—	−0.54	−0.6 Ref. 26

† Calculated from the equation: $A_c^c = I_c^c - \Delta^c$ (Δ is the forbidden gap), where $\Delta^c = 3.70$ eV.(30,31)
‡ Calculated by SCF-MO method.(32)
§ Calculated from the equation: $A_D^D = I_D^D - \Delta^D$, where $\Delta^D = 3.10$ eV.(30)

The density of structural traps as calculated from the Eq. (9) increases quickly in the vicinity of the band edge ($| E | < kT/2$). In reality these trapping states are not active because of thermal release of carriers trapped by them. It must be emphasized that only one type of lattice defects has been taken into account in the considerations presented in this paper. In a real case, however, presence of several other kinds of defects, anisotropy of molecular interactions in the crystal and thermal vibrations of molecules, neglected here, will complicate the model and may cause considerable changes in the trap distribution.

Equations (13) and (14) can be used to estimate the depth of traps formed by chemical impurities. The conclusion is qualitatively confirmed also by results obtained for perylene-doped anthracene crystals,(36) where the steady-state space-charge-limited current–voltage characteristics indicate a new kind of traps due to the presence of impurity molecules. The current-voltage dependences have found to be in a good agreement with those reported earlier for tetracene-doped anthracene crystals.(35)

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