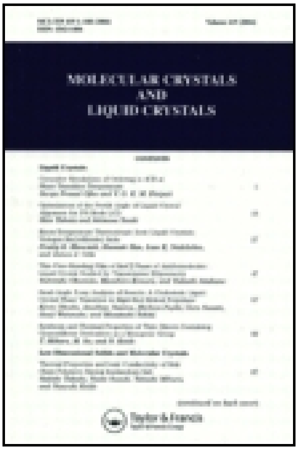

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Structural Disorder as a Source of Traps for Current Carriers in Organic Molecular Crystals

Juliusz Sworakowski [a]

[a] Institute of Organic and Physical Chemistry, Wroctaw Technical University, WybrzezCe Wyspiańskiego 27, 50-370, Wroctaw, Poland

Version of record first published: 28 Mar 2007.

To cite this article: Juliusz Sworakowski (1976): Structural Disorder as a Source of Traps for Current Carriers in Organic Molecular Crystals, Molecular Crystals and Liquid Crystals, 33:1-2, 83-89

To link to this article: http://dx.doi.org/10.1080/15421407608083873

Mol. Cryst. Liq. Cryst., 1976, Vol. 33, pp. 83–89

Printed in Holland

Structural Disorder as a Source of Traps for Current Carriers in Organic Molecular Crystals

JULIUSZ SWORAKOWSKI

Institute of Organic and Physical Chemistry, Wrocław Technical University, Wybrzeże Wyspiańskiego 27, 50–370 Wrocław, Poland

(*Received 30 July, 1975*)

Changes of the polarization energy due to presence of structural defects in a model molecular crystal and in anthracene have been calculated. The changes (which may be compared with depths of traps for current carriers) have been found to be not larger than ca. 0.5 eV. Changes of the polarization energy due to external pressures applied along principal crystallographic directions of an anthracene crystal have also been estimated. The results obtained seem to provide a support to the opinion that the formation of deep structural traps of the polarizational origin is possible only in very special cases.

1 INTRODUCTION

In 1970, two papers were published independently,[1,2] attempting to explain the mechanism of trapping of current carriers in organic molecular crystals. The approach was essentially based on the model proposed first by Lyons,[3] and suggested that any structural disorder would give rise to the appearance of traps because of local changes of the polarization energy, i.e. the energy of electrostatic interactions between a charged molecule and its polarizable environment. Qualitative estimations have demonstrated a possibility of formation of traps on (or near to) defects. The estimations were then followed by calculations carried out on a simple model lattice[4] and by preliminary computations of depths and distributions of traps associated with a partial dislocation in anthracene.[5]

All results published in the papers quoted above as well as those reported elsewhere (cf. Refs. 6 and 7) clearly indicate that certain types of defects may act as traps for current carriers. However, they appeared to be not deeper than ca. 0.5 eV, usually ranging from 0.2 to 0.3 eV, thus the results obtained could not explain the appearance of traps ca. 0.8 eV deep and deeper, commonly observed in experiments.

2 ARRANGEMENT OF MOLECULES IN IMPERFECT MOLECULAR CRYSTALS AND LOCAL CHANGES OF THE POLARIZATION ENERGY

Low values of the lattice energy in molecular crystals (usually of the order of several tens to hundreds kJ/mole) suggest that the formation of point defects should be relatively easy; there is also a number of extended defects present in those materials (see, for example, Ref. 8 and references quoted therein). Introduction of a defect may give rise to changes of positions and orientations of molecules in its vicinity and consequently leads to local changes of the polarization energy. The polarization energy itself can be calculated with a sufficient accuracy employing the procedure proposed by Lyons and his collaborators;[9] however, the calculations can be carried out only when positions of all molecules are known. In principle, the positions may be established by calculating positions of minima of the potential energy of intermolecular interactions, and for anisotropic (non-spherical) molecules the simplest way consists in calculating sums of atom-atom potentials, as first proposed by Kitaigorodskii.[10]

Preliminary calculations employing this scheme were carried out for an anthracene crystal[5] and demonstrated that the method may be used to calculate the positions and orientations of molecules near a defect. However, since most of symmetry relations are broken on introduction of the defect, and in addition the atom–atom potentials scheme multiplies the number of necessary calculations by the factor of a hundred or so,† the procedure requires a lot of computer time.

For the reasons mentioned above, it seemed necessary to deal with a crystal consisting of molecules not as composed as those of anthracene. For the qualitative discussion, a crystal built of model anisotropic "molecules" has been considered. It has been assumed that the "molecule" consists of six spherical elements (corresponding to some extent to atoms in the Kitaigorodskii's approach) placed inside an ellipsoid. For each spherical element a simple isotropic 6–12 potential has been adapted to give 100 kJ/mole for the lattice energy. Dimensions of the ellipsoids have been chosen in such a way as to imitate the shape of anthracene molecules as closely as possible.

As a first step, the structure of a perfect crystal was calculated assuming the space group $P2_1/a$. The unit cell parameters obtained from calculations

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† For example, in anthracene every single molecule–molecule interaction requires 636 atom–atom terms to be calculated.

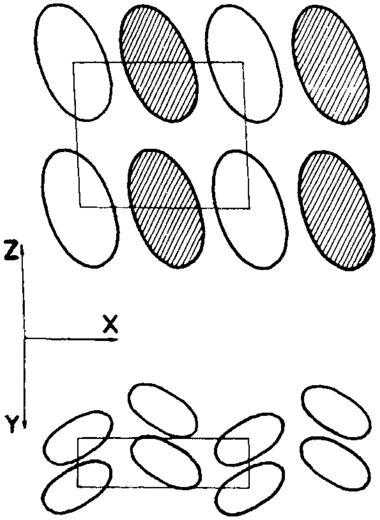

FIGURE 1 The arrangement of molecules in a perfect lattice of the model crystal.

are: $a = 1.114$ nm, $b = 0.330$ nm, $c = 0.942$ nm, $\beta = 92°42'$. The orientation of molecules is shown in Figure 1.

The polarization energy was then calculated as a sum of ion–dipole and dipole–dipole terms, interactions of 249 molecules nearest to the central one being taken into account

$$P = P_{id} + P_{dd},$$

where

$$P_{id} = -\sum_i \frac{e^2}{2r_i^6}(r_i)^T(m_i)(B)(m_i)^T(r_i)$$

and

$$P_{dd} = G^2e^2 \sum_{i>j} r_i^{-3} r_j^{-3} r_{ij}^{-3}\{(r_i)^T(r_j) - 3r_{ij}^{-2}[(r_i)^T(r_{ij})][(r_j)^T(r_{ij})]\}$$

In the above equations (r_i) and (r_j) are column matrices representing distances of i-th and j-th molecules from the ion, (m_i) is the direction cosines matrix, (B) is the polarizability matrix, and G is the average polarizability of the molecule.†

The value of the polarization energy of the perfect crystal was calculated to amount to -2.59 eV.

In the next stage, an attempt has been made to establish positions and orientations of molecules surrounding a point defect. The calculations were

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† Both (B) and G have been assumed to be identical with the corresponding values for anthracene as determined experimentally by LeFevre and Sundaram.[11]

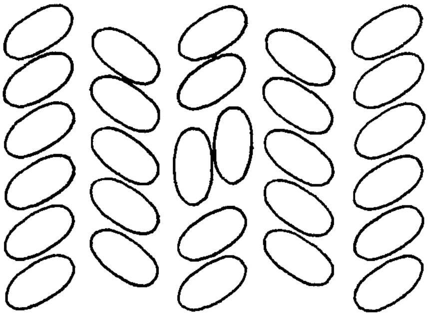

FIGURE 2 Positions of molecules on the (001) plane of the model crystal containing a point defect.

carried out employing a step-by-step iterative procedure being essentially a modification of that described in Ref. 4. The resulting molecular arrangement is shown in Figure 2. The quasi- equilibrium lattice energies of the molecules placed in the centre of the defect and surrounding it changed, and amounted to ca. −50 kJ/mole. The largest increase of the absolute value of the polarization energy (which can be compared with the depth of a structural trap) was found to be equal to ca. 0.28 eV.

It is worthy to note that the quasi-equilibrium positions and orientations of those molecules have been found to be not much different from those that could be guessed from purely geometrical considerations, and which have been chosen as starting points to the iteration. This argument may serve as a partial justification for calculating changes of the polarization energy in molecular aggregates with arbitrarily established positions of molecules.

Having this in mind, an attempt was made to compare the results obtained from calculations on the model crystal with those for anthracene, for which many experimental results are available. As an example, an edge dislocation has been considered, its core extending along the [100] direction and its Burgers vector being [010]. Positions of anthracene molecules were established arbitrarily; the resulting local changes of the polarization energy are shown in Figure 3. As one can note, the largest increase of the polarization energy amounts to ca. 0.2 eV, and this value seems to be rather overestimated since the crystal has not been allowed to relax around the defect.

Similar calculations for the model crystal have not been done; however, one may expect larger changes of the polarization energy† and in consequence deeper traps could be formed. The same would probably be true for pyrene-like crystals containing pairs of closely-spaced molecules.

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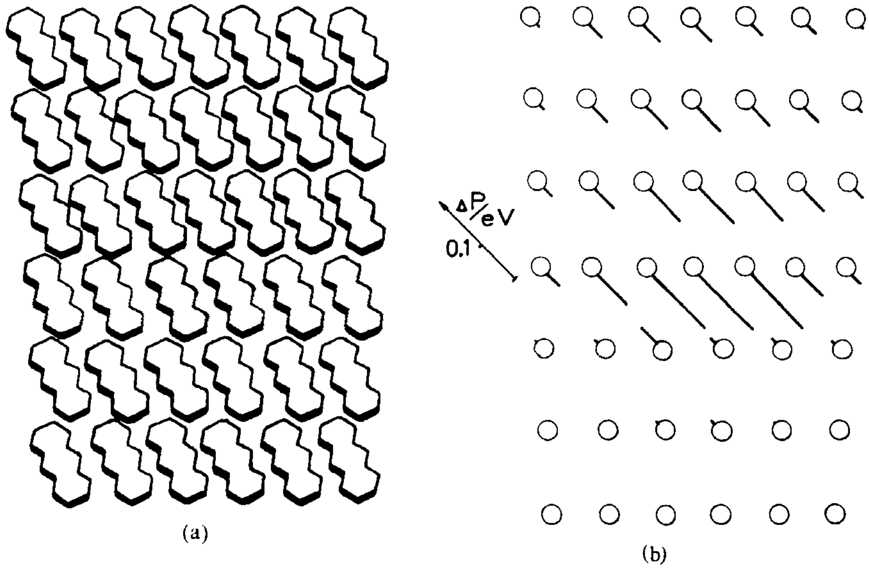
† The Burgers vector would amount to ca. 0.55 of that in anthracene, and the polarization energy should change roughly with a power of the reciprocal Burgers vector.



(a) (b)

FIGURE 3 Approximate positions of anthracene molecules near the core of an edge dislocation (a), and resulting local changes of the polarization energy (b).

3 EFFECT OF LINEAR COMPRESSIONS ON THE POLARIZATION ENERGY IN ANTHRACENE

The results of calculations described in the preceding section raise the question whether it is possible to find deeper traps which are associated with structural defects. Such a situation might take place if a substantial local contraction of the crystal lattice arises. First estimations of this effect were published by Silinsh *et al.*[6] who calculated the polarization energy to increase by ca. 0.19 eV under a uniform contraction of ca. 10%. Those calculations, however, tend to average the effect of the contraction, and a better approach to the problem may be achieved by calculating changes of the polarization energy associated with linear contractions of lattices.

Results of the calculations which were carried out for an anthracene crystal compressed along three principal crystallographic directions are shown in Figure 4. It comes from the figure that significant compressions are necessary to produce meaningful changes of the polarization energy (note the opposite direction of changes connected with contractions along the *c* axis). The situation becomes more evident if, making use of the results published by Danno and Inokuchi,[12] one calculates pressures which are necessary to change the polarization energy to a given extent. It appears that a change of ca. 0.3 to 0.4 eV would require pressures as high as several tens of kilobars to be applied.

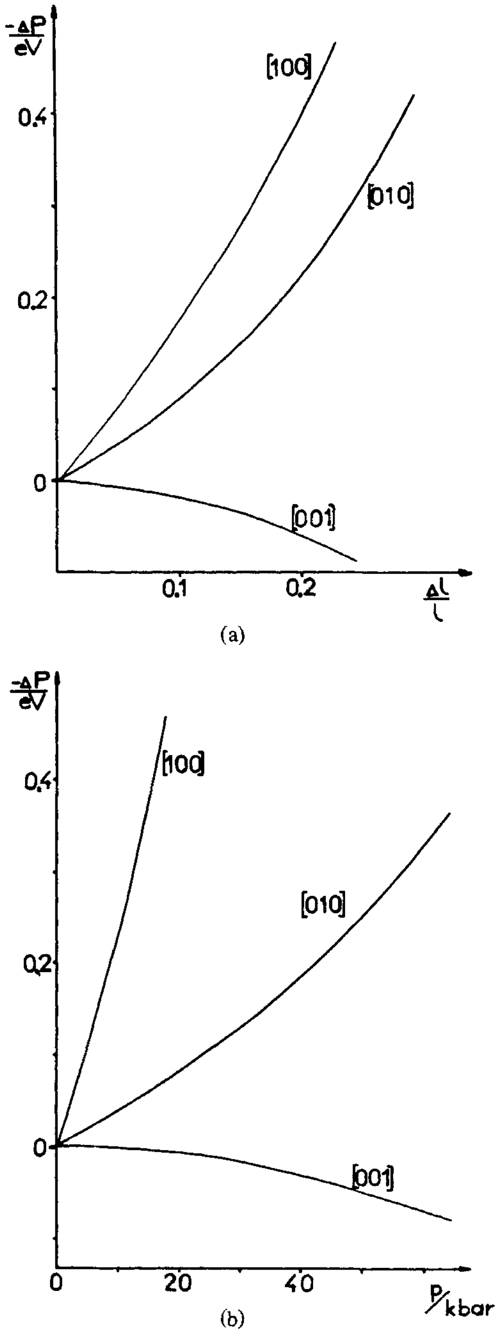


FIGURE 4 Changes of the polarization energy due to local contractions (a) and external pressures (b) applied along three principal directions.

4 CONCLUSIONS

The results of calculations reported in this paper clearly indicate that a stable arrangement of molecules which would give an increase of the polarization energy larger than ca. 0.3 to 0.5 eV may be met in anthracene and anthracene-like crystals only in very special cases. Even if such a non-equilibrium configuration of molecules could occur as a result of the crystal growth under non-equilibrium conditions, it should be rather unstable and easy to remove by annealing. Nevertheless, in the author's opinion it is rather difficult to find any type of internal strain equivalent to external pressures of the order of several kilobars.

The reasoning presented in this paper, if correct, practically eliminates a possibility of formation of traps deeper than ca. 0.5 eV by structural defects in anthracene-like crystals (although it is not impossible that such states may occur in structures similar to that of pyrene).

Acknowledgement

This work was supported by the Institute of Physics of the Polish Academy of Sciences.

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