

The Effect of Symmetry of a Molecule Electronic Density on the Dipole Moment of Unit Cell and Hole Conductivity of Thin Polycrystalline Films of Anthrone and Anthraquinone

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Our research is related to thin films of two compounds, i.e. anthrone and anthraquinone built on the basis of anthracene skeleton, with the molecular weight. for anthrone MW=194,228 g/mol and for anthraquinone MW=208,212 g/mol. Both mentioned above compounds crystallize in the nearly identical crystal lattices [1], monoclinic system with point group C_{2h}^5 and space group ($P2_1/a$) with bimolecular unit of the dimensions (at 20°C): $a_0 = (15,83 \pm 0.04) \text{ \AA}$, $b_0 = (3,97 \pm 0.01) \text{ \AA}$, $c_0 = (7,89 \pm 0.01) \text{ \AA}$, $\beta = 102,5^\circ$ for anthraquinone], and $a_0 = (15.80 \pm 0.03) \text{ \AA}$, $b_0 = (3.998 \pm 0.005) \text{ \AA}$, $c_0 = (7.860 \pm 0.016) \text{ \AA}$, $\beta = 101^\circ 40' \pm 10'$, $Z=2$ for anthrone. The main difference, essential for our studies, is the fact that the anthraquinone molecules being centrosymmetric possess small dipole moment in solution, near zero opposite to the non-centrosymmetric anthrone molecules which are characterised by large dipole moment of 3,5 D.

We have conducted two step theoretical calculations with use the convenient method used for calculating excited states TD-DFT – an extension of density functional theory (DFT). Such TD-DFT external time-dependent potentials can be considered as a weak perturbation. Using this method, the dynamic process such as transition between two eigenstates can be described. TD-DFT enables extraction of the information about excitation energies, frequency-dependent response properties and photo absorption spectra of the studied molecule. In the first stage we have used quantum-mechanical calculations for determination the electronic structure and properties of a single molecule for both compounds in the manner described in our previous paper [2]. In the second stage we have calculated the electronic structure and properties of a single crystal unit cell for both studied compounds. The results obtained in the second stage allowed us to describe intramolecular and intermolecular electron interactions for molecules situated in the equilibrium positions determined by a symmetry of the crystal unit cell and value of the dipole moment of the single molecule and the single unit cell. Based on these calculations we have tried to made an analysis useful for evaluation the experimental values of the drift mobility for both studied compounds.

Above mentioned molecular calculations allowed us to determine the dipole moment in the crystal unit cell for both considered compounds. For anthraquinone calculated dipole moment in [x,y,z] axis system has components [-0.48, -1.03, -1.70], and the value of the length of this vector is 2.04 Debye. For anthrone despite the "statistical" decomposition of molecules which is observed in the crystallographic measurements (if we take into account the direction and the sense of the C-O bond) calculations showed the presence of a significant dipole moment. This dipole moment is in relation to the axes [x, y, z] with the value of components [17.51, 3.56, -0.70] which gives a value of 17.88 Debye for the length of this vector. The value of the dipole moment in the crystalline phase for the anthrone is thus 8.8 times higher than that of anthraquinone. This is almost exactly the same numerical value which can be calculated as the higher mobility of holes in the layers of anthrone in relation to the lower mobility of holes in the layers of anthraquinone.

[1] H.D. Flack, 1970. I. Phil. Trans. A, **266**, 561 (1970).

[2] S. Kania, B. Kościelniak-Mucha, J. Kuliński P. Słoma, Sci. Bull. Techn. Univ. Lodz, Physics, **36**, 13 (2015).