Intermolecular interactions of layers
octa-phenyl-2,3-naphthalocyaninato zinc

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Abstract. The orientation of octa-phenyl-2,3-naphthalocyaninato zinc molecules is modeled
by the atom-atom potential method. The dependence of the interaction energy of octa-phenyl-
2,3-naphthalocyaninato zinc molecules on the angles characterizing their orientation relative to
each other is established. It is shown that the obtained values of the interaction energy allow
us to qualitatively explain the formation of molecules in a columnar structure.

1. Introduction
In contrast to the expensive and difficult-to-prepare silicon nanoelectronic elements, organic
materials [1–3] can be deposited by cheaper wet methods and demonstrate controlled absorption
over a wide optical range. Currently, phthalocyanines predominate in the field of modern organic
materials. They are used or potentially suitable for creating polarizing optical structures in the
form of thin-film anisotropic optical means of protection and identification of various industrial
products. An important fundamental task of great practical importance is the control of the
structure of such materials [4]. The control of the structure leads to the direct creation of thin-
film nanomaterials with optimal physical and chemical properties, which is necessary for the
creation of modern efficient nanoelectronic devices [5].

The intermolecular orientation of aliphatic hydrocarbon crystal compounds has been well
studied [6–8]. At the same time, there are few papers devoted to the orientation of disc-shaped
molecules with a macroheterocyclic nucleus.

The aim of this work is to study the intermolecular interactions of octa-phenyl-2,3-
naphthalocyaninato zinc layers. Many phthalocyanine derivatives are known as substances that
are used in organic nanoelectronics devices [4,9].

2. Simulation of materials
The structural formula and model of octa-phenyl-2,3-naphthalocyaninato zinc are shown in
Figure 1. The molecules were plotted from the coordinates of their atoms. The optimization of
the atomic coordinates in the construction of the compound under study was carried out using
the GROMACS physical and chemical modeling software package.

The mutual orientation of the molecules is determined by the angles $\theta, \varphi, \psi$ (Fig. 2), which
varied from $0^\circ$ to $180^\circ$ in increments of $10^\circ$. Here $X, Y, Z$ is the coordinate system associated
Figure 1. Structural formula of the studied octa-phenyl-2,3-naphthalocyaninato zinc

Figure 2. Mutual arrangement of the coordinates systems, connected with the molecule (1, 2, 3) and the surface (x, y, z). θ – the polar angle of axis 1 in the system x, y, z; ϕ – the azimuth of axis 1 (the angle of the surface xz with 1z); θ is the polar angle of the axis 1 in the fixed coordinate system; ϕ is the azimuth of the axis 1 (the angle between the planes XZ and 1Z); ψ is the azimuth of the mobile system (the angle between the planes 1Z and 12).

The initial value of the distance a from the center of inertia of the molecule to the plane passing through the centers of inertia of the atoms composing the surface was taken to be 3 Å and the energy was minimized along the height a.

The calculations were carried out using atom–atom potentials method [10–12]. The interaction energy is shown as a sum of energy of interaction values between the atoms of the molecule and the atoms of the crystal surface, which is determined by the correlation
Figure 3. The dependence of the interaction energy of the octa-phenyl-2,3-naphthalocyaninato zinc system on the orientation angles $\theta, \varphi$, at $\psi=30^\circ$ (a), and the orientation angles $\theta, \psi$, at $\varphi=10^\circ$ (b).

(Lennard–Jones potential)

$$E = \sum_{i,j} E_{i,j},$$

$$E_{i,j} = 4\varepsilon \left( \frac{\sigma}{r_{i,j}} \right)^{12} - \left( \frac{\sigma}{r_{i,j}} \right)^{6}$$

in which $\varepsilon > 0$ – depth parameter, $\sigma$ – distance between certain atoms, at which $E_{ij} = 0$; $r_{ij}$ – the distance between the atom surface $i$ and the atom of the molecule $j$.

The interaction energy was determined by the ratio (1), where the values of the interaction parameters for the groups C’...C’, N...N, H...H were taken from [13]. The interaction potentials, C’...H, and C’...N were calculated by us from the well-established principle of additivity of Van der Waals radii and the geometric mean rule, and are given in [12]. It can be noted that with these values of atom–atom potentials, the orientation values of liquid crystal octyl cyanobiphenyl molecules on the surface of graphite and polyethylene crystals were obtained [14][16], which have a good agreement with the experimental data [8][13].

Conclusions

As a result, the dependence of the interaction energy of the octa-phenyl-2,3-naphthalocyaninato zinc molecules on the orientation angles $\theta, \varphi, \psi$ was obtained.

From figures 3 it can be seen that the energy of the intermolecular interaction of octa-phenyl-2,3-naphthalocyaninato zinc molecules significantly depends on the three orientation angles $\theta, \varphi, \psi$, while there is a region of orientation states of naphthalocyanine molecules, the interaction energy of which is an order of magnitude greater than the energy of the other states.

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