

# МЕТОДЫ ИССЛЕДОВАНИЯ НАНОСТРУКТУР И НАНОМАТЕРИАЛОВ

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## SUPRAMOLECULAR ORGANIZATION AND ELECTRONIC STRUCTURE OF PERYLENE TETRACARBOXYLIC DIIMIDE: X-RAY DIFFRACTION AND THEORETICAL STUDIES

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**Key words:** liquid crystals, X-ray diffraction, non-covalent interactions, electronic properties, molecular dynamics, quantum-chemistry calculation

*The inter- and intracolumnar arrangements of the perylene tetracarboxylic diimide (PDI) was investigated experimentally and theoretically by using X-ray diffraction with combined DFT computation and molecular dynamics simulation. The structure was found to be hexagonal with a packing parameter of nearest column  $a = 2.025$  nm characterized by a  $\sim 45^\circ$  twist of molecules within the columns.*

In the last years the self-assembly of organic molecules presented the perspectives of developing novel materials for electronics. A special attention was made on the mesophases, characterized by p-conjugated molecules and formation of columnar superstructures in both the solid and liquid crystalline states. The arrangement of the molecules allows a charge carrier transport along the one-dimensional structures by increasing of coupling of p-electrons, which make them unique materials for device applications, such as field-effect transistors and solar cells. The perspectives of such materials became clear taking into account the anisotropy of electronic properties, low-cost and facile device fabrication, self-healing of defects within the columns, and relatively high local one-dimensional charge carrier mobility [1].

Most of the alkyl substituted low molecular weight species which organize into columnar superstructures are p-type semiconductors. Rylene diimide molecules, such as perylene tetracarboxylic diimide (PDI), terrylene tetracarboxylic diimide (TDI) and quaterrylene tetracarboxylic diimide (QDI) form a unique class of n-type organic semiconductors [2]. Both n- and p-types molecules can be used separately in field-effect transistors, while only their mixture are required in bulk-heterojunction photovoltaics, like hexabenzocoronene (HBC)-PDI and polycarbazol

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(CPz)-PDI, revealed the highest efficiencies for columnar phases [3]. PDI derivatives are used to control the molecular deposition [4], as an injector of charge carriers for different polymers employing the time-of-flight technique [5], and as fluorescence switch [6]. Furthermore, perylene has been utilized as convenient precursor for a consequent synthesis of more complex molecules, such as terrylene derivatives [7], perylenebisimide and bisbenzimidazole [8], fullerene-perylene and perylenebisimide-triphenyldiamine dyads [9]. These substances are widely used for optoelectronic applications [5–10] owing to their dyes cover the visible light [11] and due to their high thermal and photostability [12]. Nevertheless, the supramolecular structure into which PDI self-assembles is not yet fully understood. An intracolumnar arrangement was proposed with a twist of the adjacent molecules [11, 13], or without any twist [14]. A detailed knowledge about the supramolecular organisations is necessary for the calculation of the electronic properties, since the electron and hole transfers strongly depend on the molecular arrangement [15].

The aim of this communication is to determine the supramolecular structure of heptyloctyl substituted PDI (1), namely inter- and intracolumnar arrangements by using both X-ray diffraction analysis and simulations.

Molecular dynamics simulation (total 30 ns run) had been done at a pressure  $P = 0.1$  MPa and a temperature  $T = 300$  K by using usual OPLS force field. GROMACS [20] software was used. The equations of motion were integrated using Varlet's algorithm with a time step of 2 fs. After constructing topology of single PDI molecule, a periodic box of  $4 \times 4 \times 12$  molecules with hexagonal arrangement of columns with a  $45^\circ$  twist within columns were created. DFT calculations (BH&H/6–31G(d) level of theory) were done for dimers constructed from optimized monomers at the fixed distance of 0.35 nm between molecular cores. Gaussian 03 and GAMESS software were used. The total energy and electronic spectra were calculated with for different rotational angles.

2D-WAXS experimental setup [1, 11] consisted of a rotating anode (Rigaku 18 kW) X-ray beam with a pinhole collimation and a 2D Siemens

detector, that use a double graphite monochromator for the  $\text{Cu-K}_\alpha$  radiation ( $\lambda = 0.154$  nm).

The two-dimensional wide-angle X-ray scattering (2D-WAXS) pattern of a mechanically aligned PDI (1) is presented in Fig. 1. On the basis of two distinct equatorial reflections an orthorhombic intercolumnar arrangement was previously proposed with a unit cell of  $a = 1.67$  nm and  $b = 2.08$  nm. Later it is possible to consider the unit cell as a hexagonal lattice with  $a = 4.05$  nm [11] leading to the assignment of the two equatorial reflections as (110) and (200).

The intracolumnar packing is more complex and can be characterized by the meridional reflections. The major distinct (004) wide-angle meridional reflection is related to the  $\pi$ -stacking period of 0.345 nm, as shown in Fig. 1. The molecular cores arrange orthogonally with respect to the columnar axis. The appearance of additional (001) meridional reflections suggests a further intracolumnar correlation. Taking into account the  $\pi$ -stacking distance in relation with the high order distance of 1.39 nm, it is derived that

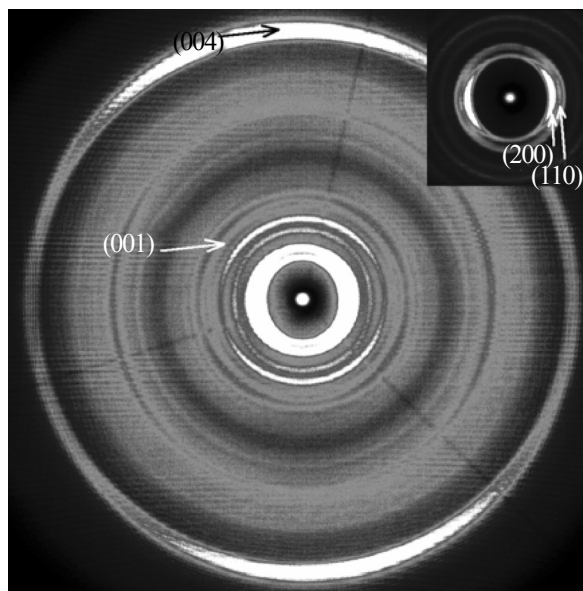


Fig. 1. The 2D-WAXS pattern of PDI (1) at a temperature  $T = 300$  K. Two meridional (004) and (001) reflections correspond to 0.345 nm and 1.39 nm periodicities in a direction of the columnar axis. Inset highlights the two major (110) and (200) equatorial reflections of hexagonal intercolumnar arrangement of  $a = 4.05$  nm

every fourth molecule within the column is in the same position and laterally rotated by  $45^\circ$  to each other, providing the excellent agreement with  $\pi$ -stacking distance of  $1.39/4 = 0.3475$  nm with a divergence average of less than 1%.

The large hexagonal packing parameter of  $a = 4.05$  nm contradicts the theoretical size of the PDI (1) molecules, while orthorhombic one with  $a > b$  parameters disagrees with the possible  $45^\circ$  twist of molecules. In comparison, the more extended rylene molecules, i.e. TDI and QDI revealed even a smaller hexagonal lattice with  $a = 2.94$  nm and  $a = 3.09$  nm, respectively. It is reasonable to assume that the parameter of  $a = 4.05$  nm involves every second column leading to a simple intercolumnar distance of 2.025 nm in the hexagonal unit cell. Indeed, such a non-usual distribution of reflections with absence

Table 1. Experimental (WAXS) and simulation data for a PDI columnar phase at 300 K

Method	Intercolumnar distance, nm	Intracolumnar distance, nm	Rotational angle, deg
Experimental	0.345	2.025	45
Simulation	0.35	1.98	40–45

of the (100) reflection has been reported for discotic liquid crystals [16] and fullerene-like crystals [17]. In such a case PDI belongs to columnar liquid crystals with  $p6$  mm symmetry, like other rylenes.

In order to confirm the experimentally observed hexagonal packing of columns, molecular dynamics (MD) simulation was performed (see for details [18]). As a test, a single column of 12 molecules was simulated. During the simulation the column was tilted in the simulated box, already indicating rather a hexagonal than rectangular or orthorhombic

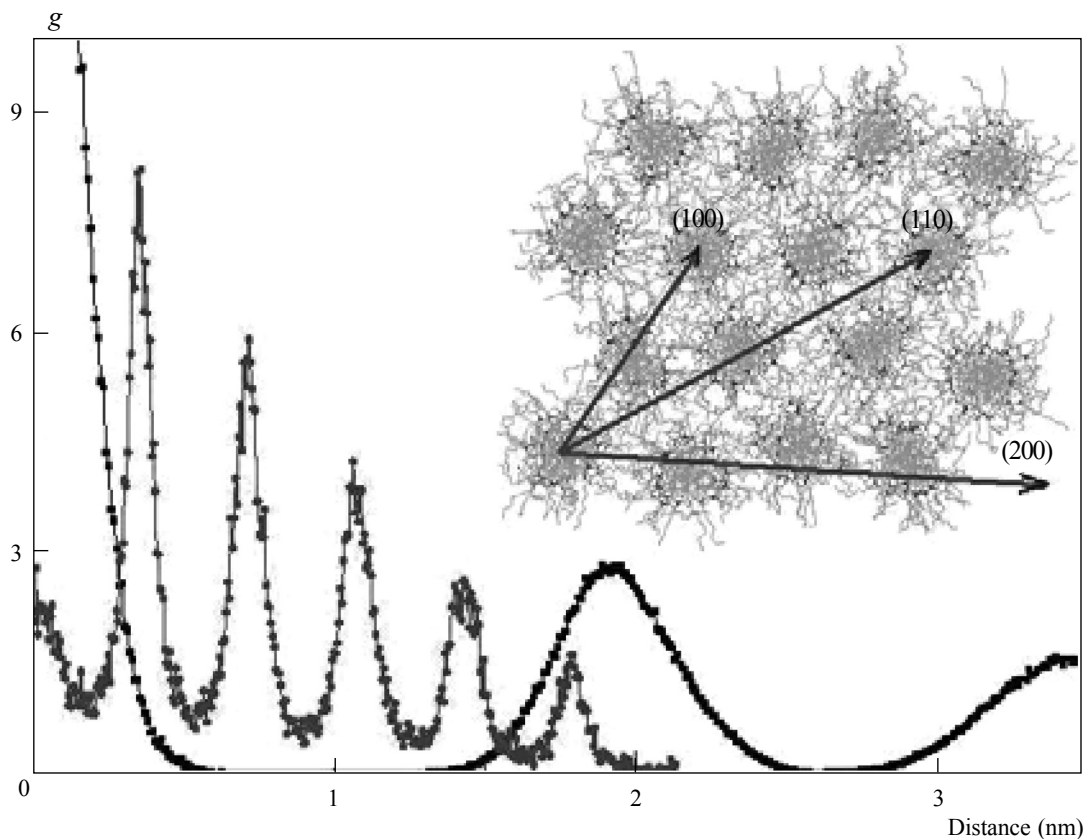


Fig. 2. Calculated positional correlation functions: perpendicular (squares) and parallel (circles). Inset highlights the hexagonal columnar arrangement of a simulation box after 30 ns run

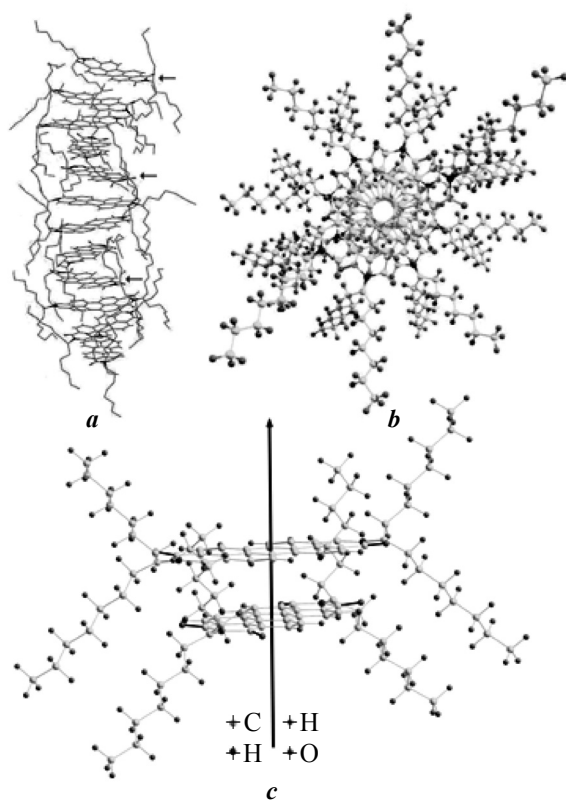


Fig. 3. The single column of simulated box after MD simulation (a). Molecular architecture of PDI (1) molecules in the stack (every molecule is rotated to its neighbour by  $45^\circ$  around the columnar axis as shown by arrows) (b). Geometry of dimer of PDI molecules (at  $30^\circ$ ) during quantum-chemistry calculations (c)

columnar arrangement. MD simulations revealed a unit cell parameter of 1.98 nm and a  $\pi$ -stacking distance of 0.35 nm (Fig. 2 and Fig. 3a) which were in a good agreement with the experimental values, from above discussed X-ray diffraction analysis. The hexagonal structure was slightly disordered so that the (100) reflection entirely could not be visible.

The packing of PDI molecules in the columns revealed strong dependence on the molecular rotational angle, see Fig. 3b. At the  $0^\circ$  angle, i.e. only translations without twist, appropriate branches of dimer tails were closely connected with each other. Thus, a rotation of tails and a tilting of molecules were expected in order to minimize a total energy within the columns as shown in Fig. 3c. The total energetic profiles for different dimers with

$D_{6h}$  and  $D_{3h}$  symmetries revealed that the global energy minimum was rather unpredictable [15]. Fig. 4 shows the dependence of the total energies for PDI (1) and hydrogen substituted PDI (2) dimers calculated with BH&H/6-31g(d) method without optimisation at the fixed intermolecular distance of 0.35 nm. This method was successfully tested for calculation of vdW interactions on benzenes and pyridines [19]. The results indicated that the global energy minima for PDI (2) dimer were disposed in the  $\sim 30^\circ$  and  $\sim 150^\circ$  rotational angle position. At the  $90^\circ$  there was also a local minimum (see Fig. 4) for both types of dimers.

For PDI (1) dimer the evolution of the total energy was more complicated with non-symmetric dependence on the rotational angle. The absolute minimum of function equals to  $\sim 24^\circ$ . The local minimum equaled to  $\sim 139^\circ$  (see Fig. 4), corresponding to  $\sim 41^\circ$  twist, in full agreement with experimental value. It was expected the helical arrangement of molecules on the values of both minima, i.e., the absolute minimum at  $\sim 24^\circ$  also might be achieved during slow crystallization process. The helical stack of the single column is reproduced in Fig. 3a and Fig. 3b. Comparisons of the WAXS experimental data with the simulations are shown in the table 1. The comparison shows

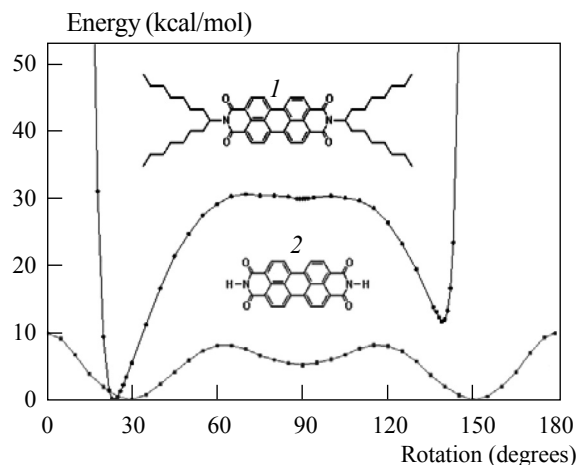


Fig. 4. Evolution of a difference of the total energies of a dimer made of  $D_{2h}$  symmetry PDI-C<sub>8,7</sub> (1) (circles) and  $D_{2h}$  symmetry PDI-H (2) (squares) when rotating one core along the stacking axis, as calculated at DFT (BH&H) level of theory

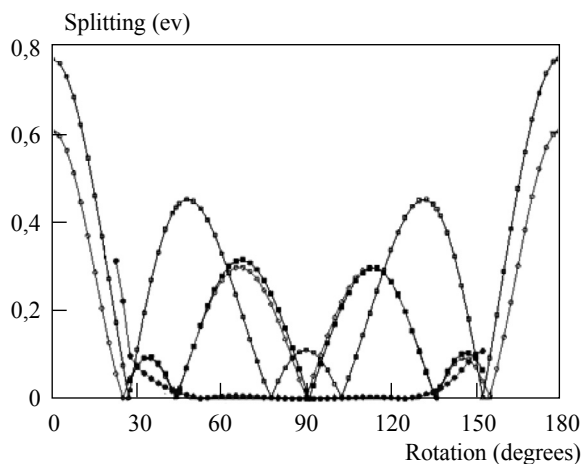


Fig. 5. Evolution of the HOMO (squares) and LUMO (circles) splittings of PDI (1) (filled types) and PDI (2) (open types) dimers when rotating around the stacking axis

that simulations fully agreed with experimental data and the structure of PDI is determined.

Fig. 5 shows the results of the HOMO and LUMO splittings calculations, which are the double from the intermolecular transfer integral ( $t$ ). As clearly seen, the electronic structures of PDI derivatives strongly depends on the substitutions: the alkyl chain causes a change of geometry that leads to distortion of the electronic structure. In particular, the dependence of HOMO splitting of PDI (1) and LUMO splitting of PDI (2) are practically identical. The dependence of splittings on the angle is non-symmetric, according to slight twisting of molecular skeletons in order to balance the massive branches of opposite alkyl chains. The rate of electron hopping ( $k$ ) depends on LUMO splitting as  $k \sim t^2$  [15]. Thus, PDI electron mobility equals to zero for the PDI (2) at the  $45^\circ$  experimental twist angle, while the perylene derivative carrying the branched side chains reveals the relatively high  $t$  values of  $\sim 0.01$  eV (Fig. 5). Thereby, substitution of branched tails has a strong influence on the charge carrier mobility as major factor, besides angle of twist, temperature and defects. The calculated value of  $t$  at  $\sim 25^\circ$  angle is  $\sim 0.1$  eV. Reorganisation energies for PDI equals to 0.18 eV and 0.20 eV for positive and negative

polarons, respectively, which are very close to the HATNA energies of 0.1–0.2 eV. According to the Marcus formalism [15] the charge transfer rate and charge mobility for PDI at the absolute minimum position are expected to be comparable with that of HATNA derivatives, promising electron transporters.

In summary, the molecular and supramolecular arrangement has been determined for columnar phase of a perylene derivative bearing branched alkyl substituents. Analysis of 2D-WAXS patterns clearly indicated a hexagonal arrangement of columns and a helical packing of the molecules within the columns, like other rylene mesophases. Molecular dynamics simulation confirmed the stability of the hexagonal intercolumnar structure with a packing parameter of  $\sim 2$  nm and  $\pi$ -stacking distance of  $\sim 0.35$  nm. The helical intracolumnar arrangement of molecules was also verified by the DFT calculations. The calculated optimal rotational angles were proved to be  $24^\circ$  and  $41^\circ$  with the last value been very close to the experimental value of  $45^\circ$ . The electronic spectra revealed an essential dependence from the nature of the tails: the substitutes (tails, rings etc.) must be taken into account during transfer integral and charge mobility calculations.

Меж- и внутрикільончаті упорядкування перилена були досліджені експериментально і теоретично при використанні рентгеновської дифракції з комбінованими обчисленнями методами функціонала густини та молекулярної динаміки. Структура кристалла визначена як гексагональна з упаковочним параметром самої близької колонки  $a = 2,025$  нм з характерним твістом  $\sim 45^\circ$  молекул в межах колонки.

**Ключові слова:** рідкі кристали, рентгеновська дифракція, нековалентні взаємодії, електронні властивості, молекулярна динаміка, квантово-хімічні обчислення

Між- і внутрішньокільончаті впорядкування перилена було досліджено експериментально й теоретично при використанні рентгеновської дифракції з комбінованими обчисленнями методами функціоналу густини та молекулярної динаміки. Структуру кристала визначено як гексагональну з пакувальним параметром найближчої колонки  $a = 2,025$  нм із характерним твістом  $\sim 45^\circ$  молекул у межах колонки.

**Ключові слова:** рідкі кристали, рентгеновська дифракція, нековалентні взаємодії, електронні властивості, молекулярна динаміка, квантово-хімічні обчислення

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