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Crystals of the phenazine coordination polymer with the third order symmetry axis: formation, properties

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Unusual quasi-two-dimensional crystals of a regular triangular shape, self-formed in the process of obtaining a coordination polymer based on phenazine and silver, are described and studied. X-ray diffraction studies were carried out, the interplanar distance was determined, and the spectra of Raman scattering were obtained. A mechanism is proposed that can cause the appearance of triangular crystals from nuclei of hexagonal symmetry.

Keywords: X-ray diffractometry, Raman scattering, phenazines - organic crystals.

Introduction

The control of a process of obtaining crystal forms of nano-sized items is of large interest because it is a nano-sized scale where the properties of the items start largely depend on their sizes and forms. We can mention the change of the catalyst activity of the nanoparticles of noble metals depending on the shape [1], the efficiency of various kinds of nuclei for the kinetics and form genesis at the subsequent crystallization [2–4].

The phenazine (Phz) $(C_6H_4)_2N_2$ is an initial agent for obtaining many chemicals including biologically active and medicine drugs, so its derivatives and the properties thereof are intensely studied [5,6]. Coordination polymers (CP) of phenazine with silver, which are described in the present study, are of interest in terms of catalysis, sensorics [7] and biomedical applications as antivirus and antibacterial materials [5]. And due to the high electric conductivity properties in combination with micro sizes of the particles with quite narrow size distribution, these compounds are a promising material for the high-tech print method of obtaining the electronic devices [8].

A fundamental aspect of this issue is at least of the same interest. Usually, the habitus of the crystals corresponds to one of the symmetry subgroups of the crystal lattice. The majority of found symmetrical crystals is described by the cubic or hexagonal symmetry [9]. As far as the authors know the regularly triangular crystals are extremely rare and researchers have recently focused their attention on these cases [10–12].

When the triangular crystals are purposefully produced, for example, of the semiconductor materials, one uses specially cut substrates [12], which provide the necessary symmetry. In some other cases, when the triangular crystal-lites spontaneously grow in the isotropic conditions (in the solutions), the triangle shape provides some compromise between the low symmetry of the initial molecules/blocks and anisotropy of the growth rates [10, 13–15]. The present study is dedicated to detection and study of the properties of quasi-two-dimensional triangular crystallites of the phenazine-silver coordination polymers.

1. Synthesis and composition of the crystallites of the polymer phenazine

The phenazine molecule is quite simple and symmetrical, and it can be considered as a derivative of anthracene [16]. The anthracene molecule is comprised of three benzene rings, which are mated with faces of aromatic hexagon so that all the three rings are arranged along one direction. The phenazine molecules have three similar hexagonal rings, but in this case the carbon atoms of free apexes of the middle ring are replaced with nitrogen atoms. It is known that there are substances which are produced by replacing the same apex atoms of carbon with oxygen, sulphur [17].

The neutral and oxidized phenazine molecule is designed as shown on Fig. 1.

The availability of nitrogen causes phenazine activity in the chemical reactions. Even when applying small oxidation potentials ($\sim +0.5\,\text{V}$), one of the nitrogen atoms gives off
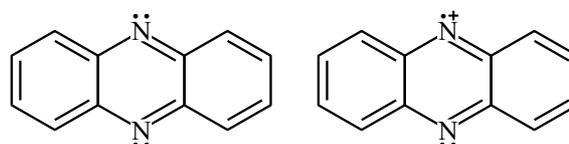
Figure 1. Neutral and oxidized phenazine molecule.

(to the Ag^+ cation, in our case) one of the two „unpaired“ electrons [18]. As a result, the molecule obtains a positive charge to become a stable cation-radical (the „unpaired“ electrons of the nitrogen atom are dotted on Fig. 1; the so-called Kroger-Vink designation [19]). According to the existing concept, the oxidized form participates in polymerization. The positive charge being generated in oxidation of the phenazine molecule at one of the nitrogen atoms is compensated by a closely located counter ion. In this case, the counter ion is an anion (NO^{3-}) of the molecule of silver nitrate. According to the existing concept, it is the oxidation process that starts a phenazine self-organization process with CP formation [20–23].

For the phenazine and its derivatives, it is known that there are the coordination polymers with Hg^{2+} [20], Cu [21,22], Ni [23], Ru [24] and other transition metals. At the same time, usually, the said studies do not specify a form of chemical bond of the metal atom in the CP. Quite often, the metal, which combines the organic molecules into the coordination polymer of the various structure, is silver. This element has 10 *d*-electrons and is characterized by a large variety of generation of coordination bonds. The coordination polymers containing silver are distinguished by a coordination number, i.e. the number of the involved d-electrons, and a structure [25].

The present study has obtained the phenazine and silver polymer during a two-stage process being continuously performed in one reactor. The initial agents included aniline as a phenazine synthesis precursor and the silver nitrate $AgNO_3$ taken in excess to the aniline. At the initial stage, by the impact of Ag^+ in combination with an accompanying oxidizer (oxygen) the bond of the ortho-$C-H$ aniline is activated, thereby resulting in the oxidation cascade process of cyclization of the two aniline molecules with formation of the phenazine molecule. At the same time, the two silver ions recover to a metal [26]. Then, the generated phenazine, whose reaction medium solubility is small, participates in the self-organization process with excessive silver nitrate. Thus, the second stage generates the coordination polymer in the course of the one-pot continuous process.

The CP was synthesized in an aqueous-organic media at 20 and at $40°C$ with constant bubbling through the reaction medium. The molar containment of the initial agents was: the aniline $(0.1 M)$ (as the phenazine obtaining precursor) and the silver nitrate was $1/2.5–3.5$. Initially, the agents were completely dissolved, but with time a CP suspension was formed within the reaction phase. The final product was output by filtering, intensely flushed with water to remove unreacted the silver nitrate and the aniline, and then dried at the normal conditions. After drying, the product was a yellow-brown powder, its output in relation to the weight of loaded agents was $30–35\%$. The preliminary spectrum studies (the analysis of the absorption spectra) have shown no phenazine or polyaniline in the obtained material as possible intermediate reaction products. The obtained coordination polymer was well dispersed in water with formation of a stable dispersion.

The composition of the organic part of the product was specified by the elementary analysis method using Elemental Analyzer VARIOEL III (Elementar, Germany). The elementary composition of the organic part of the synthesized samples: carbon $60–63\%$, nitrogen $12–14\%$, hydrogen $3–4\%$ and residual oxygen $19–20\%$, which is well consistent with the formula of the oxidized phenazine molecule (C 60%, N 13%, H 3.3%, O 19.8%), containing the NO_3^- group as the counter ion.

The silver content in total both in a metallic and ionic state was determined by burning out the organic part of the sample at the temperature above $600°C$ in the air atmosphere. The silver content in the synthesis products is $63–65\%$ or $3.5–3.8$ of the Ag atom for the molar fraction of phenazine. In accordance with the stoichiometry of the initial stage, it should be expected that the CP composition has 2 moles of metal silver per 1 mole of phenazine, and the metal silver is recovered when oxidizing the aniline to the phenazine. The excessive $AgNO_3$ participates in the subsequent interaction with phenazine, in a coordinating way bonding the organic molecules into arranged micron-sized structures. Thanks to the simultaneous processes of synthesis of phenazine with release of the metal silver and the self-organization of phenazine in the coordination polymer, these structures are filled with the metal silver as an impurity (guest) element to have the high electric conductivity. Thus, the obtained product should be classified as a metal-organic matrix or, in order words, categorized as a coordination polymer.

2. Morphology of the crystals of the phenazine-based polymer

Crystals of the neutral phenazine of the standard agent (Fluka), which are not oxidized, belong to the monoclinic crystal system. Nevertheless, during the microscope study of this material we observed some filament crystals. These filament crystals have been observed earlier and were interpreted as the crystals of the oxidized phenazine [27].

The obtained phenazine coordination polymer samples have exhibited quasi-two-dimensional (plate-like) crystals of a regularly triangular shape. The crystals are clearly seen in the optical microscope (the habitus of the produced crystals will be discussed in this study later). The appearance of the crystals is shown on Figs. 2 and 3. The crystals are sized within a range of several microns. An opaque material, which can be distinguished on the optical image (Fig. 2) and scattered among the triangular crystals, is the metal silver recovered from the oxidizer Ag^+ when obtaining the phenazine from the aniline. The availability of the significant content of the metal silver is confirmed by the high electric conductivity of the obtained coordination polymer (above $10^3\ \Omega^{-1}\cdot cm^{-1}$).

The image of the synthesis products obtained by the scanning electron microscopy (SEM) using the microscope Carl Zeiss Supra 55 VP, also confirms the flat triangular
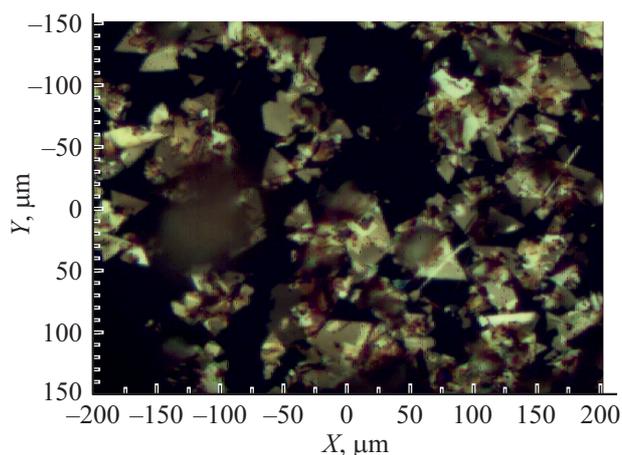
Figure 2. Optical micro-image of the triangular crystals.
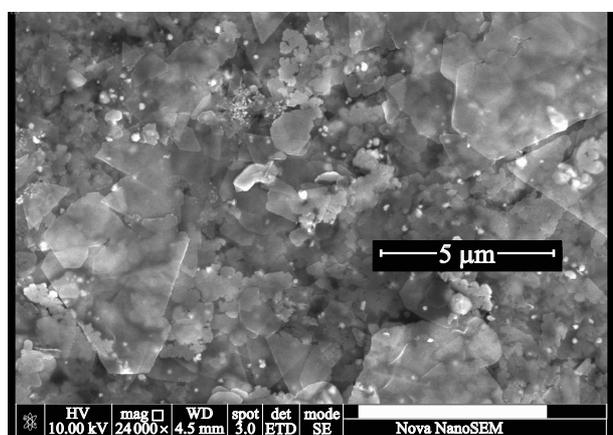
Figure 3. SEM-image of the triangular crystals.

crystals present in the reaction products. The SEM image (Fig. 3) explains a small thickness of such crystals showing underlying layers to be seen through the triangular crystal scales on the shown image.

3. X-ray diffraction analysis (XRD)

The X-ray diffraction studies have been performed in an X-ray diffractometer DRON UM 1.0 designed to operate in the two-crystal mode of the extended base with recording the scattered radiation by an SCSD-4C detector (Single Channel Scintillation Detector with COM interface (RadiconSPb)). The scattered radiation was automatically recorded step by step.

For the measurements, the reaction product was dried in a thin layer on an amorphous substrate, which implied a predominant orientation of the crystals in parallel to the substrate.

The experiments have used the monochromatic Ge 111 radiation Cu $K_{\alpha 1}$, $\lambda = 1.54056$ Å. The XRD data were recorded in the reflection mode. With such an experimental
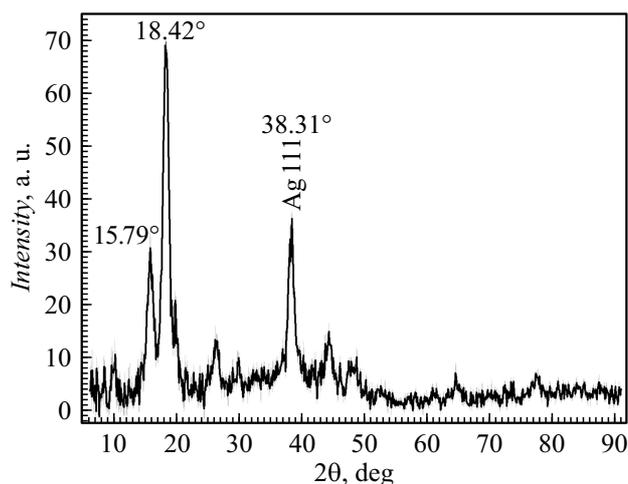
Figure 4. The XRD curve from the studied sample at the Cu $K_{\alpha 1}$ radiation. The positions of the most intense lines were additionally given.

setup, the line positions of the diffraction reflection curves (DRC) provide information on the interplanar (and, possibly, interlayer) distance of the quasi-two-dimensional crystals [28]. In order to evaluate the synthesis reproducibility, the studies were performed on several samples obtained during the experiments at the various temperatures.

The diffraction reflection curve is shown on Fig. 4. The exact line positions and the lattice periods corresponding thereto are shown in Table 1.

As noted, in the realized experimental setup the DRC provide the information on the interplanar (interlayer) distance in the studied quasi-two-dimensional crystals. In [29], the peaks in the lines 7–10 are identified as the phenazine lines. However, these lines quite well match the tabular values for the diffraction reflection lines (of the high orders) of the silver crystals [30], i.e. the said lines can correspond to the crystals formed during recovery of the metal silver along with the CP synthesis processes. The table lines 1–4 do not correspond to the tabular values of the silver line positions and cannot be attributed to the crystal silver. At the same time, the lines 1–4 in the table have quite big intensity comparable with the intensities of the silver crystal lines. This fact implies that the reflection is provided by the silver atoms included in (or localized on) the plane of the CP quasi-two-dimensional crystals. Checking this assumption will require additional studies.

4. Inelastic (Raman) light scattering

The inelastic light scattering was recorded using the micro-Raman analysis equipment MRS-320 HORIBA-Yobin-Ivon with excitement of the scattering by the light of the He−Ne-laser with the wavelength of 632.81 nm. The test lateral resolution was $3-5\,\mu$m, thereby recording the spectra of light scattering from separate crystals. In order to isolate separate crystal exemplars, the post-reaction mass

Table 1. Observed DRC peaks and the crystal lattice parameters corresponding thereto

N	2Θ	d (Å)	Intensity (relative units)	
1	15.79	8.79468	35	
2	18.42	7.53432	70	
3	19.75	7.03639	25	
4	26.31	5.2902	15	
5	29.93	4.65523	10	
6	38.31	3.6505	38	Ag 111
7	44.36	3.15834	15	?...Ag 200
8	48.1	2.91797	8	
9	64.6	2.19369	8	?...Ag 220
10	77.5	1.84606	7	?...Ag 311

was dispersed in water; then a drop of the diluted dispersion was dried on a glass or metal substrate. It enabled operating separate crystals. (In contrast to XRD, wherein the intensity of X-ray radiation scattered on a unit organic crystallite does not exceed the level of instrument noise.)

The recorded spectra can have two ranges marked, namely, the region of $1100-1800$ and the region of $400-600 \, \text{cm}^{-1}$.

The first one of the said regions records a group of lines corresponding to molecular oscillations, which could be modified by the crystal environment.

Figure 5 shows the spectra within the region of $1100-1800 \, \text{cm}^{-1}$ for several triangular crystals obtained at the various temperatures. It is clear that the spectra are still similar in general, which should be manifested at the common structural base of the phenazine, i.e., the three combined aromatic rings. The experimentally obtained spectra are somewhat different in small details. It can be assumed
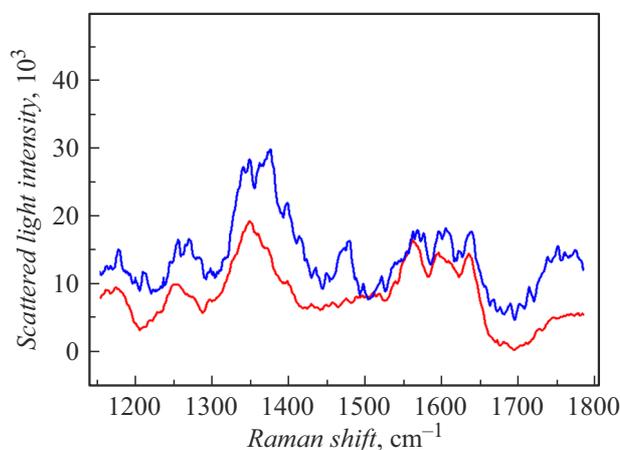
Figure 5. Spectra of inelastic light scattering within the region of $1100-1800 \, \text{cm}^{-1}$ from the two triangular crystals, being the same in outward appearance, but obtained at the various synthesis conditions.

Table 2. Comparison of the lines in inelastic light scattering by the triangular CP crystal and the phenazine filament crystal

Triangular crystal	1178	1252	1273	1348	1560	1593	1632	1755
Filament crystal	1173	1251		1348	1562	1603	1634	1750
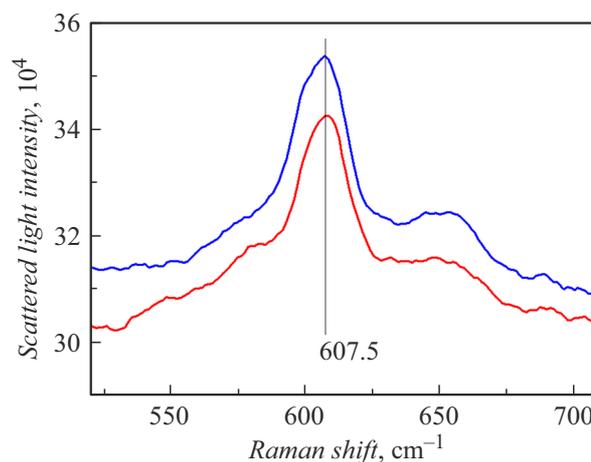
Figure 6. Spectra of inelastic light scattering within the region of $400-800 \, \text{cm}^{-1}$ from the two triangular crystals, being the same in outward appearance, but obtained at the various synthesis conditions.

that these differences are caused, inter alia, by possible mismatch of crystal orientations when recording the spectra.

The most meaningful bands in the spectra of this region are about $1170 \, \text{cm}^{-1}$; $1240-1250 \, \text{cm}^{-1}$; $134 \, \text{cm}^{-1}$ (intens.); $1477 \, \text{cm}^{-1}$ (sometimes without it); the three bands of the approximately equal intensity and close in the position — about 1560, 1600, $1632 \, \text{cm}^{-1}$; as well as the band $1750-1760 \, \text{cm}^{-1}$.

For comparative analysis, one has recorded the spectra of the neutral phenazine crystals (Fluka), as well as the crystal filaments found among the phenazine crystals in the same agent (the existence of the filament crystals formed by the oxidized phenazine is described in the study [27]). By the structure of the band of $1100-1800 \, \text{cm}^{-1}$, the spectra of the studied triangular crystals exhibited a substantial match to the spectra of the phenazine filaments (Table 2). It is known that the phenazine can be oxidized by air oxygen (the oxidation potential $+1.23 \, \text{V}$) [31]. This process is minimized in a dry condition and accelerated in the solutions. Apparently, the dispersion of the agent prior to preparation for spectrum recording resulted in partial phenazine oxidation and its aggregation. The authors regard these facts as a confirmation that the obtained coordination polymer is formed by the oxidized phenazine, because that are the oxidized phenazine molecules that tend to the aggregation with formation of structures of the various type.

Besides, the spectra of the obtained coordination polymer were compared with spectra of other substances containing the mated aromatic rings, which would be in sediment as a result of reaction byproducts: naphthalene, anthracene, aniline, polyaniline. The comparison was partially by the literature data, and partially by spectra experimentally obtained by us from the said substances. The comparison sample spectra also contain the line group within the region of $1100-1800\,\mathrm{cm}^{-1}$. However, by the band structure the spectra of these materials had little match to the spectra of the studied crystals.

In our opinion, particular interest should be paid to the scattering spectra within the region of $400-800\,\mathrm{cm}^{-1}$ (Fig. 6). The triangular crystals have exhibited a clear line within the region of $607.5\,\mathrm{cm}^{-1}$ (Fig. 6). It should be noted that being quite intensive, this line is distinctly exhibited on weakly structured background and recorded in all the experiments of observing the inelastic scattering in the triangular crystals. There is no similar line in other substances taken by us for the comparative analysis; the similar line is not detected in the published studies.

We should make an emphasis on the position of this line ($607.5\,\mathrm{cm}^{-1}$). It is located substantially lower in terms of the energy (more than two times) in comparison with the lines of the molecular oscillation group. It assumes either participation of a heavy weight in this oscillation, or a substantially weaker bond of the oscillating element. The reaction mixture had a heavy atom (ion) — silver with the weight of 108 at.u. The ratio of the mass of this atom to the masses of other atoms, supposedly included in the crystal, is almost one order-of-magnitude. And at the equal bond force, the line of oscillations of the fragment coupled with the silver atom could be within the region of about $600\,\mathrm{cm}^{-1}$. For comparison, it should be noted that, for example, for the silver iodide (AgI) containing the heavy anion (I^-), too, the main group of the lines lie around $110\,\mathrm{cm}^{-1}$ [32]). It is possible that the studied compound, in which silver is together with relatively light carbon atoms, can have an oscillatory mode around $600\,\mathrm{cm}^{-1}$.

Another possible interpretation: this line can correspond to some mode of the interplanar oscillation between relatively weak-bonded planes of the molecular crystal. In this case, the oscillation frequency must be less sensitive to the availability of impurities and local defects of the structure. This assumption well agrees with the coincidence of the positions of the line $607.5\,\mathrm{cm}^{-1}$ for all the studied samples. We note that both specified assumptions on the nature of the line $607.5\,\mathrm{cm}^{-1}$ do not exclude each other.

In the course of the experiments it was noted that the line $607.5\,\mathrm{cm}^{-1}$ is decreasing in its intensity in long illumination, while the intensity of the wider band sharply increased around $295\,\mathrm{cm}^{-1}$. As it is known, the majority of the silver-containing salts exhibit photosensitivity. In our case, we have not noticed the decrease in the intensity of other lines except for $607.5\,\mathrm{cm}^{-1}$. By analogy, this observation confirms that silver is a component of the CP being the material of the triangular crystals.

Taking into account the set of all the experimental facts, the observation of the line $607.5\,\mathrm{cm}^{-1}$ within the spectrum of light scattering by the triangular crystals is unambiguously indicative of presence of internal ordering, including an ordered arrangement of silver. The noted photosensitivity of the line additionally confirms that the silver is in the crystal lattice, i.e. the detected crystals are metal-organic polymers based on phenazine and silver.

5. Possible mechanisms of formation of the crystals with the C_3 symmetry

The shape of the synthesized quasi-two-dimensional crystals is unusual. As it is well clear from the images of electron (SEM) and optical microscopy, they are quite perfect flat and, apparently, equilateral triangles, with sizes from a micron to a dozen microns, i.e. quite macroscopic objects.

The observation of these objects raises some questions: why the symmetry of these crystals is different from the symmetry of the internal structure elements (phenazine)? The type of the phenazine symmetry (and mating thereof) is a sixth-order axis, whereas the appearance of the crystals corresponds to the reduced C_3 symmetry. What growth mechanism accounts for such reduced symmetry?

It can be assumed that the hexagonal nuclei can transform into the triangular crystals due to the anisotropy of the transport fluxes of a crystallizing substance. As mentioned, the combination of the phenazine molecules into the 2D-polymer is caused by a bond though the counter ions — NO_3^- anions. Due to the localized charges of the counter ions, the crystal nucleus can have an electric field. This one will be substantially higher near the apexes of the crystal nucleus than near the faces thereof. In turn, the electric field near the apexes is a factor of amplification of drift of the molecules having a dipole moment towards the nucleus apexes.

Material flows for crystallite growth

Growing layers
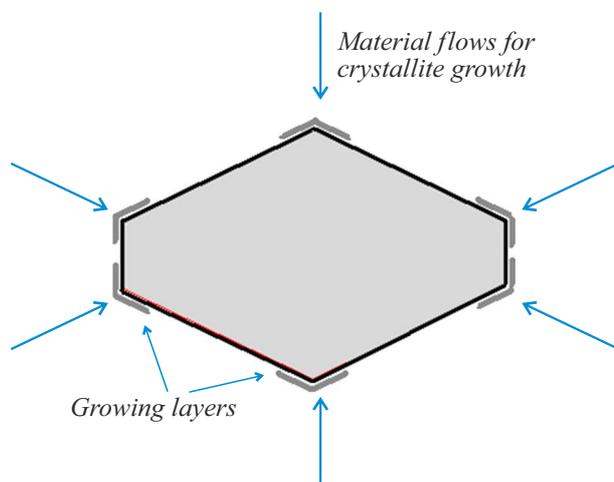
Figure 7. Illustration of the growth mechanism for the triangular crystals.

In other words, the described mechanism is not a proper one of the crystal growth, but in a microscope scale it provides for predominant influx of the material to the apexes of a growing crystallite. The subsequent mechanism of the crystallite face growth is not so significant. The faces can continue to grow, for example, by a step advancement mechanism. It is important for our hypothesis that the growth process is fed up with a material from the apexes of the crystal nucleus.

The process of formation of the crystallites is illustrated on Fig. 7. With such a growth mechanism, when the crystallization material is fed up from the hexagonal apexes, the narrower faces will occlude faster and, finally, they can occlude by transforming the face into the apex. Thus, the mechanism amplifying the mass transfer near the apexes of the crystal nuclei can ensure reduction of the symmetry of the initial hexagonal nuclei. The direction of the predominant growth can be selected by an insignificant initial asymmetry of the nucleus shape or the crystallization conditions. We have not found the proposed mechanism in the literature.

The micro-electron image (Fig. 3) can be used to see a crystallite in a transition form as an imperfect rhomb with angles around $60°/120°$. It well illustrates the proposed mechanism additionally. The possibility of existence of such a mechanism is also specified in data of the study [33], which evidently show organic crystallites as quadrangular plates being close in shape to quadrates, but deformed (oblong) towards the apexes.

Conclusion

This study reports the synthesis and the investigation of the CP crystal properties based on the phenazine. The observed crystals are flat formations shaped as regular triangles and, apparently, having a thickness of several molecular layers. The ordered internal structure is confirmed by the spectra of combination scattering of these crystals and the X-ray diffraction data. It has proposed the mechanism which can cause the reduction of the crystal symmetry C_6 corresponding to the symmetry of the structural elements to the symmetry C_3 describing the habitus of the detected crystals.

Conflict of interest

The authors declare that they have no conflict of interest.

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