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# Direct Observation of Structure Change in Ni–Phthalocyanine Caused by Iodine Doping

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## Abstract

The nonstoichiometric compound $C_{32}H_{16}I_xN_8Ni$ ($x \leq 1{\cdot}0$) [$Ni(phc).I_x$] has been studied by high-resolution electron microscopy. The mechanism of the topotactic formation was revealed by the use of two kinds of epitaxial films taking different orientations. The local changes of the molecular orientations of Ni(phc) induced by iodine doping were observed and the effect of the substrate on the axial correlation between the original and the complex crystal is discussed on the basis of the molecular interaction force of the adsorbed molecules on the substrate.

## Introduction

Though a crystal structure can be fully analyzed by X-ray diffraction, the method is of no practical use for the study of the structure of an aperiodic material or of a disordered state in a crystal. In contrast, high-resolution electron microscopy has the ability to analyze the structures of such materials. In the last ten years the resolution of electron microscopes and observation techniques have been so much improved that even molecular images of organic substances can be observed in thin crystalline specimens and some results have been reported by the present authors and their co-workers (Uyeda, Kobayashi, Ishizuka & Fujiyoshi, 1978–1979, 1980). They have demonstrated that the method is very useful for the study of molecular orientation around crystal defects (Kobayashi, Fujiyoshi & Uyeda, 1982) or in crystal nuclei where the molecules deviate from the regular periodic arrangement in the crystal (Kobayashi, Fujiyoshi, Iwatsu & Uyeda, 1981).

On the other hand, the injection of different kinds of atoms or molecules into a crystal is well known as a useful method for changing its electrical properties. However, the local changes in the crystal structure induced by doping a small amount of foreign material have not been considered, even when the band structure, which strongly depends on the periodicities of atom or molecular arrangements in the crystal, should be discussed in order to interpret the change in the electronic state on doping.

The present investigation was performed in order to determine the local structural changes of Ni–phthalocyanine [abbreviated hereafter as Ni(phc), Fig. 1] introduced by iodine doping and to reveal the structure of the intermediate state in the formation of Ni(phc)–iodine complexes. The formation mechanism of a highly conductive organic crystal produced by solid–vapor reaction will be discussed on the basis of the high-resolution electron microscope observations.

## Experimental

Some needle crystals of Ni(phc) were obtained by sublimation in reduced nitrogen gas flow according to the general procedure for the purification of phthalocyanine compounds (Moser & Thomas, 1963). Thin crystalline films of Ni(phc) were prepared epitaxially by vacuum condensation of the material onto a cleaved face of mica and KCl kept at a constant temperature of 453 K in a vacuum of $1 \times 10^{-5}$ Pa. The crystal of KCl cleaved in air was degassed by baking at 823 K in the same vacuum for 2 h before deposition of Ni(phc). Some of the films on the substrates were sealed in a glass tube with a piece of iodine crystallite for several hours or a whole day at room temperature. Ni(phc) contacted with iodine vapor was reinforced by evaporating a thin carbon film indirectly onto it, stripping off the substrate in pure water and fixing it on a gold-coated microgrid for the observation of high-resolution images and electron diffraction patterns. Another part of the Ni(phc) film reinforced with carbon was doped after stripping off the substrate in order to examine the effect of the substrate on the structure of the doped crystals. The electron microscope used was a JEM-200CX equipped with a high-resolution pole piece for an objective ($C_s = 0{\cdot}8$ mm, point-to-point resolution = $2{\cdot}0$ Å) and operated at an

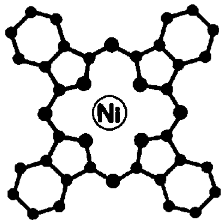

Fig. 1. The molecular structure of Ni(phc).

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accelerating voltage of 200 kV. The electron optical magnifications were 170 000 and 220 000. The minimum-dose system (Fujiyoshi, Kobayashi, Ishizuka, Uyeda, Ishida & Harada, 1980) was used for reduction of the radiation damage by the electron beam. The film thickness was monitored with a quartz-crystal microbalance and controlled to have a mean thickness of less than 100 Å on mica and 200 Å on KCl. The crystal grew homogeneously to form a continuous film on mica whereas on KCl it grew as islands. Therefore, in the latter specimen the amount of deposition should be increased in order to increase the number of particles in the observed area. In this case, however, the crystal is wedge-shaped and the thin edge parts were suitable for high-resolution observations.

## Results

An electron micrograph of the original Ni(phc) film grown on the mica surface and its high-resolution electron diffraction pattern are reproduced in Fig. 2(*a*, *b*). They show that the film is composed of laminar crystallites oriented in three directions according to the crystallographic symmetry of the mica surface. One of the present authors and his co-workers have reported the epitaxial growth of some kinds of metal–phthalocyanines on mica (Uyeda, Ashida & Suito, 1965) as well as on various kinds of alkali halides (Ashida, Uyeda & Suito, 1966) and the Ni(phc) examined here also showed the same features as with Cu(phc) or Pt(phc), as reported in previous papers. The direction of the long axis of each crystallite coincides with the *b* axis. The *b* axis with a lattice period 3·80 Å agrees with the axis of the molecular columns in which the planar molecules of Ni(phc) are closely packed facing parallel to one another, tilting slightly against the axis. Although the tilting angle projected onto the (100) film plane can be derived from the diffraction pattern, it can also be determined more obviously by the direct observation of molecular images taken with the high-resolution electron microscope. The micrograph shown in Fig. 3 reveals the orientation of the molecules in the crystal. The direction of the *b* axis is indicated by an arrow along which molecular columns lie in parallel with a regular interval of 13 Å. In each column many strips can be observed and the interval between neighboring strips is 3·80 Å as measured along the column axis. This value corresponds to the lattice period of the *b* axis as has been indicated by the electron diffraction pattern. Each strip represents an image of an Ni(phc) molecule viewed nearly along the molecular plane. The strips subtend an angle of +16 or −16° with the column axis. A schematic projection of this crystal is shown in Fig. 4 where each molecule is represented by a strip.

A high-resolution electron micrograph and the electron diffraction pattern (Fig. 5) show that the treatment of Ni(phc) with iodine vapor for several hours entailed some changes in the lattice dimensions of the crystal. The change on mica occurs without altering the orientations of the principal axes. The axial correlation between the matrix and the treated

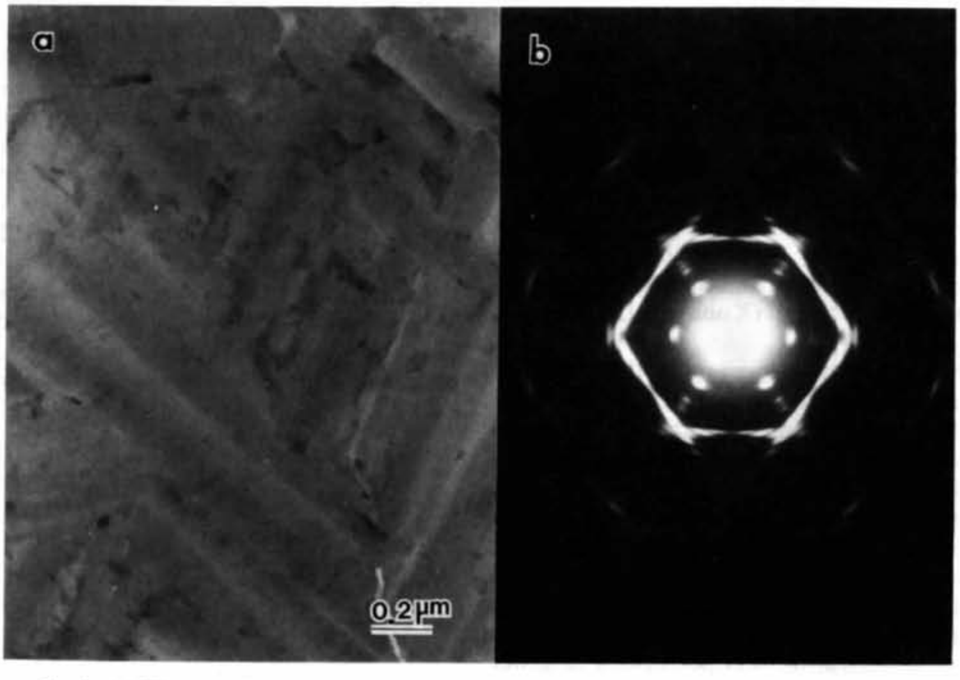


Fig. 2. (*a*) Electron micrograph and (*b*) high-resolution diffraction pattern of Ni(phc) film.

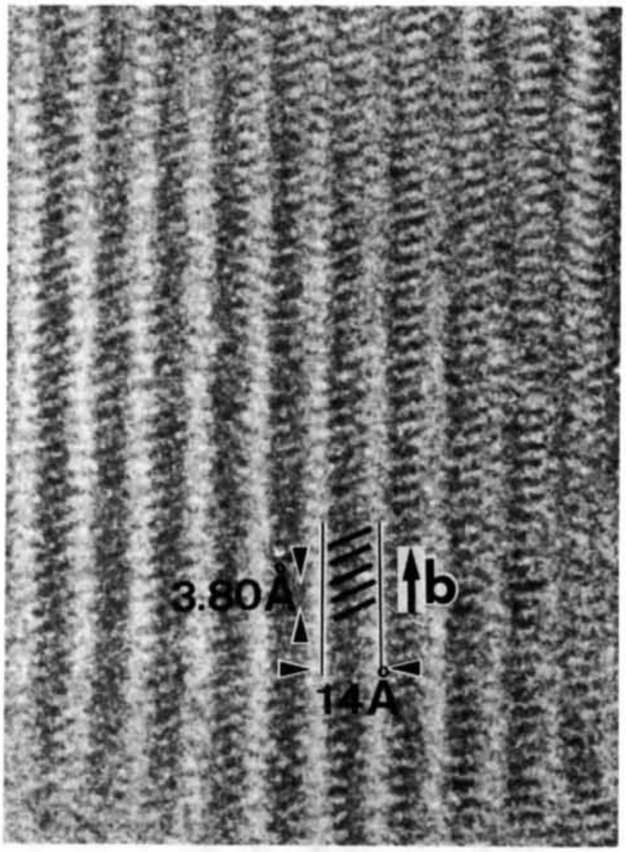


Fig. 3. A high-resolution electron micrograph of Ni(phc) grown on mica.

crystal is illustrated in Fig. 6 where for simplicity a single orientation was extracted. The fiber period of the crystal has been shortened from the original 3·80 to 3·25 Å by the treatment. In contrast, the other lattice dimension perpendicular to the fiber axis has expanded to 14 Å which is 1 Å longer than the original. A certain amount of Ni(phc) was left intact under this reaction condition. Electron micrographs of Ni(phc) film before and after contact with iodine vapor on a mica substrate are shown in Figs. 2(*a*) and 5(*a*). The micrograph of the treated sample shows strong diffraction contrast which was not observed in the images of the original specimen. The images of the lattice along the fiber axis are also clearly observed in an enlarged image of Fig. 5(*a*) as reproduced in

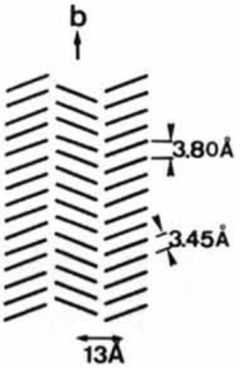


Fig. 4. A schematic representation of the molecular packing in Ni(phc) film grown on mica.

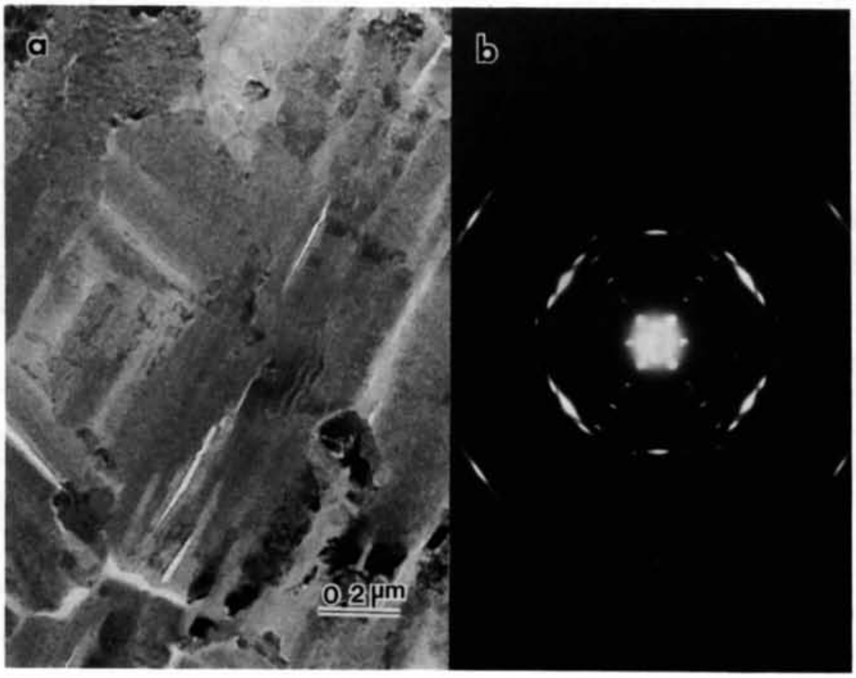


Fig. 5. (*a*) Electron micrograph and (*b*) high-resolution diffraction pattern of Ni(phc) contacted with iodine vapor.

Fig. 7. The remarkable difference between the treated and untreated samples can be recognized. By the treatment the lattice fringes which are straight in the original crystal become crooked and sometimes appear broken as was observed in the high-resolution images. The electron micrograph with higher resolution is reproduced in Fig. 8 which shows that Ni(phc) molecules are packed along these lattice fringes forming molecular columns where the molecular planes are almost perpendicular to the column axis. As mentioned before, the molecular planes in untreated Ni(phc) make an angle of ±16° with the column or fiber axis. The treatment with iodine vapor changes the angle to perpendicular to the column axis. As a result the distance between the molecular columns increases and the intermolecular distance along the column axis decreases as shown schematically in Fig. 9. These facts agree well with the predictions of the diffraction pattern shown in Fig. 5(*b*).

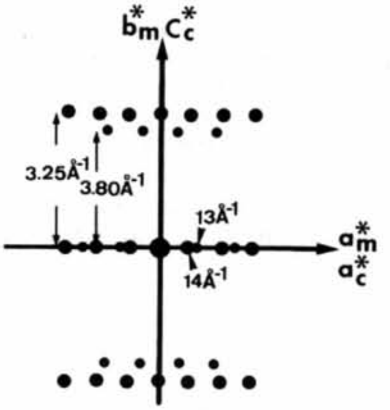


Fig. 6. A schematic representation of the axial correlation between the original Ni(phc) and the iodine-doped crystal in reciprocal space.

The epitaxial film of Ni(phc) formed on a KCl (001) face is different in shape and orientation from those on mica. Fig. 10(*a*) is the electron micrograph of Ni(phc) grown on KCl at 453 K. The crystal is a wedge-shaped dendrite and the selected-area diffraction pattern of this crystal shows that the crystal main axis is oblique to the incident electron beam. The

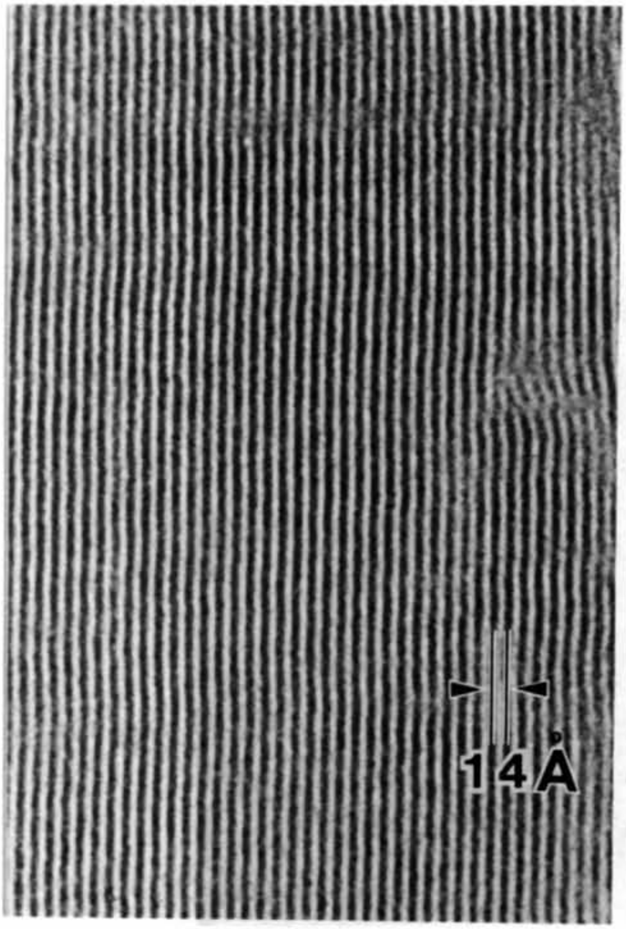


Fig. 7. Electron micrograph of the iodine-doped Ni(phc) crystal.

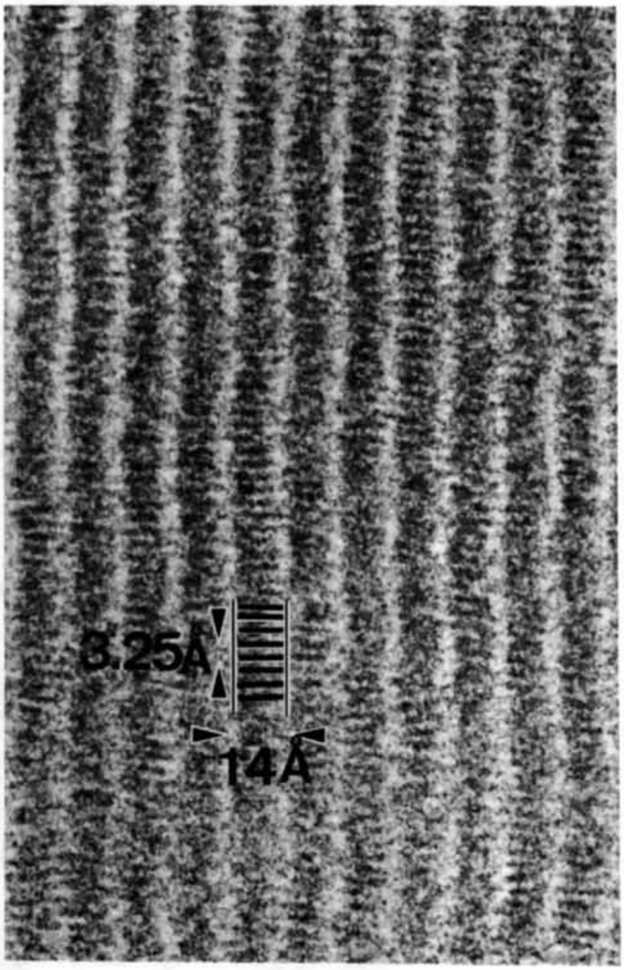


Fig. 8. Molecular images of Ni(phc) contacted with iodine vapor.

analysis of the diffraction pattern given in Fig. 10(*b*) has been fully performed by Ashida (1966*a*, *b*) who showed that the molecular columns stand with respect to the film plane and make an angle of 64° with the substrate. This situation is depicted in Fig. 11 with another model proposed by Kirk (1968). The electron micrograph is in general a projection of the three-dimensional structure along the incident electron beam which is perpendicular to the film-surface plane. Therefore, if one intends to observe the molecular images in this crystal, one should tilt the specimen so that the column axis coincides with the direction of the incident electron beam.

When this kind of crystal is treated with iodine vapor for several hours, it also changes its structure. The electron diffraction pattern reproduced in Fig. 12(*b*) shows a basal plane of the reciprocal-lattice net of a newly resulting crystal with some reflection spots from a small amount of unreacted Ni(phc) indicated by arrows. The periods of the net are 14·0 × 14·0 Å. The arrowed spots are those from the $(40\bar{2})$ plane of the original Ni(phc). The diffraction indicates that the change in crystal structure due to the reaction with iodine brought the molecular column perpendicular to the substrate and the projection of the molecular images along the column axis was observable. A high-resolution electron micrograph has proved that the column axis is parallel to the projecting axis. Fig. 13 is the image in such a projection. Here an image projected along the molecular column can be seen in a square which corresponds to the unit cell. Fig. 13(*b*) shows the molecular arrangements in the crystal and crystal boundaries. The newly resulting structure can be depicted as shown in Fig. 14 together with that of the original structure. The axial correlation between the matrix and the complex crystal revealed by electron diffraction (Fig. 12*b*) is that the [210] axis of the newly formed crystal is almost

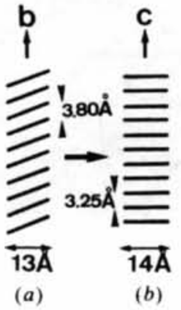


Fig. 9. The change in molecular stacking from (*a*) the original to (*b*) iodine-doped crystals reacted on mica.

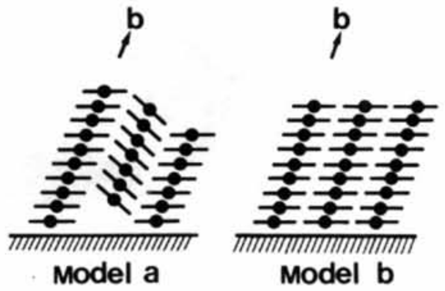


Fig. 11. Molecular orientation of Ni(phc) on KCl (*a*) after Ashida and (*b*) after Kirk.

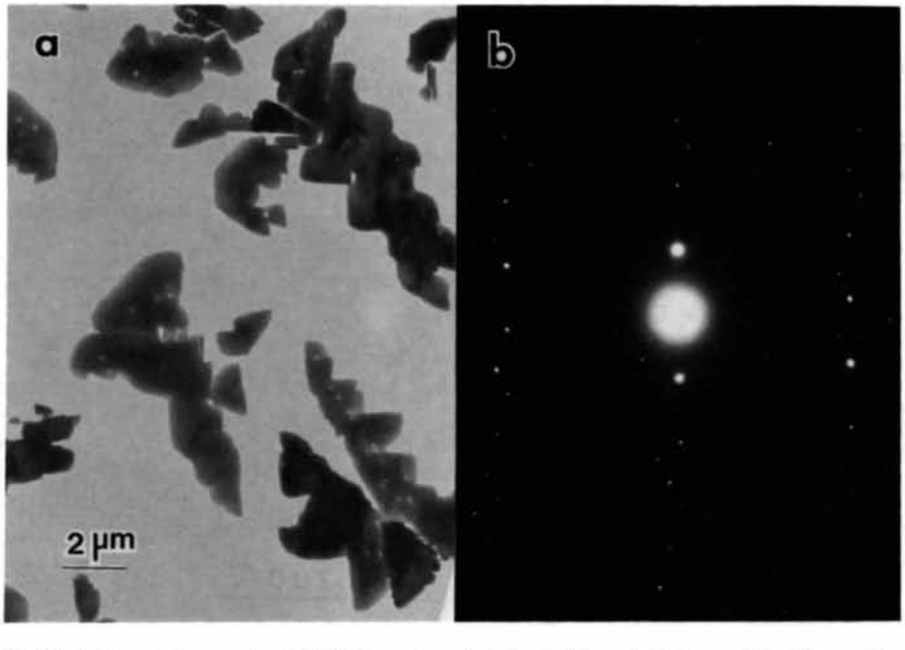


Fig. 10. (*a*) Dendrite crystal of Ni(phc) grown on KCl and (*b*) a selected-area diffraction pattern.

parallel to the [40$\bar{2}$] axis of the original crystal. This fact is explained more clearly in Fig. 14. The lines $XX'$ and $YY'$ in the figure indicate the (210) and (40$\bar{2}$) planes respectively. The molecules represented with dotted lines in (*b*) are on the substrate and they keep their original orientation (*a*) on reaction. This fact is essential for topotactic solid-state reaction. In Fig. 13(*b*) one can see grain boundaries and some other defects. The great difference between topotactic reaction mechanisms of iodine doping into Ni(phc) films grown on mica and on KCl described above lies in the fact that in the latter case the direction of the molecular column axis changes from the original ones as illustrated in Fig. 14.

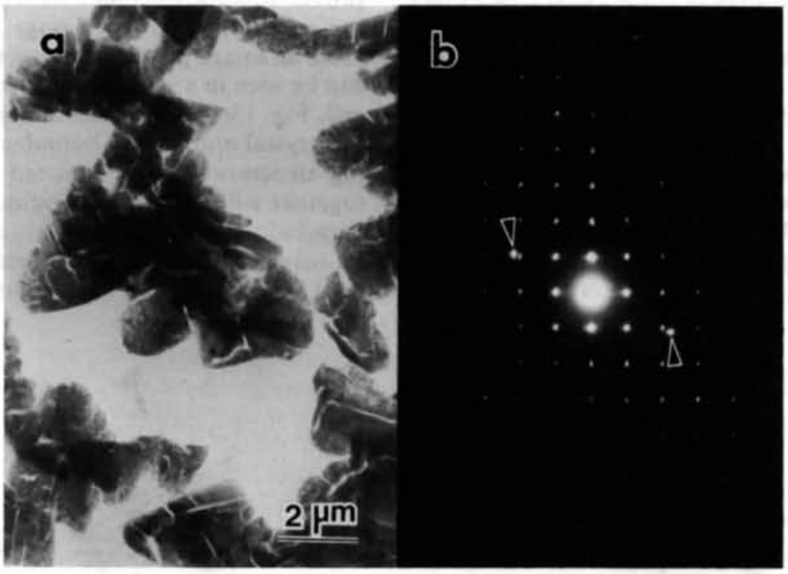


Fig. 12. (*a*) A general view of the iodine complex of Ni(phc) reacted on KCl and (*b*) a selected-area diffraction pattern.

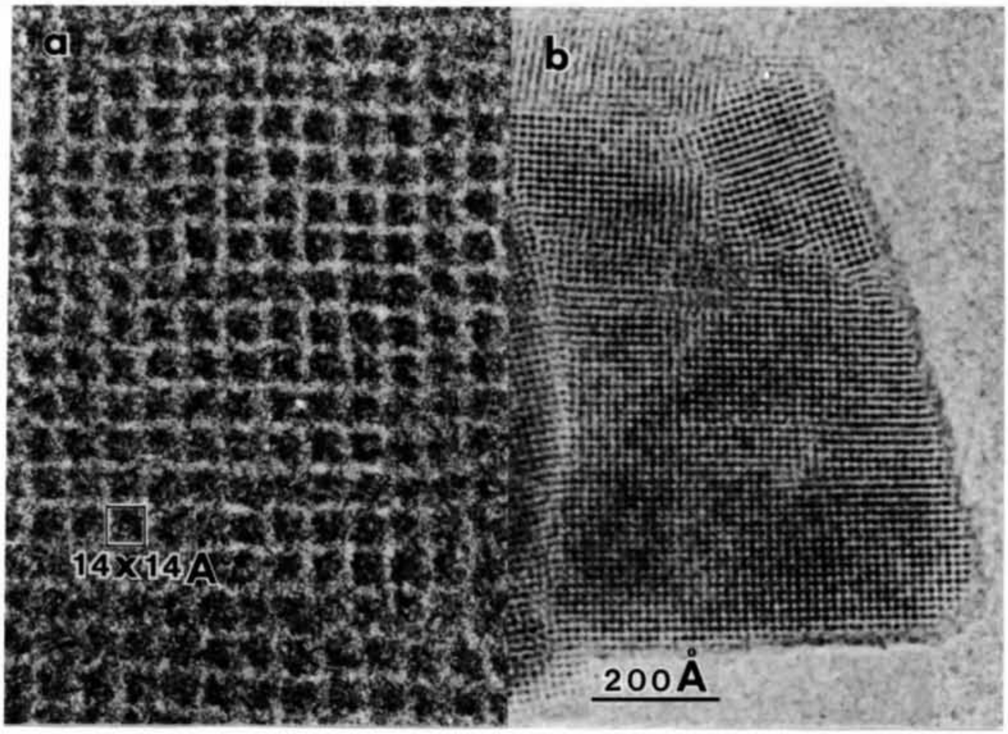
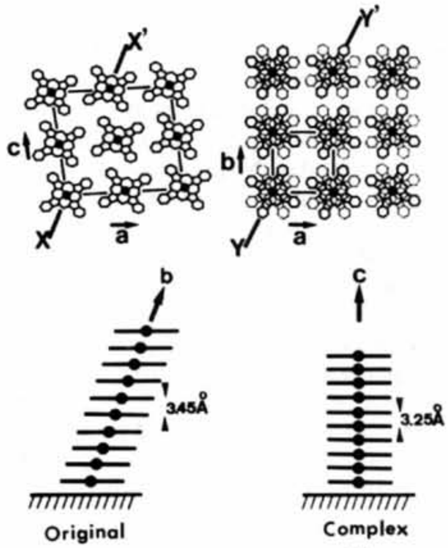


Fig. 13. (*a*) A high-resolution electron micrograph of Ni(phc) treated with iodine vapor. Each dot in (*b*) corresponds to a molecular image.

## Discussion

The reaction of Ni(phc) with iodine has recently been reported by Schramm, Stojakovic, Hoffman & Marks (1978) and Schramm, Scaringe, Stojakovic, Hoffman, Ibers & Marks (1980). They have analyzed the crystal structure of the stoichiometric complex whose composition is Ni(phc).$I_{1\cdot0}$. At the same time they showed that doping of a small amount of iodine also made the crystal of Ni(phc) very highly conductive. The conductivity of pure Ni(phc) at room temperature is $10^{-11}$ S $cm^{-1}$ whereas Ni(phc).$I_x$ ($x = 0\cdot5$–$1\cdot5$) has values of 0·7–0·8 S $cm^{-1}$. The conductivity, however, did not show any remarkable dependence on the iodine content $x$. The crystal structure analysis of this stoichiometric complex ($x = 1\cdot0$) reported by Schramm *et al.* (1980) reveals the unit-cell dimensions of this crystal to be $a = b = 13\cdot936$, $c = 6\cdot488$ Å and the space group *P4/mmc*. Ni(phc) molecules are stacked so as to form molecular columns which run parallel to the *c* axis. The molecular plane of each Ni(phc) is perpendicular to the column axis differing from that in the original untreated Ni(phc) crystal. The present results clearly demonstrate the difference in the packing manner of the molecules before and after the reaction. When the tilted molecules in the columns of pure Ni(phc) change their orientation on iodine doping, the distance between the centers of neighboring molecules, Ni–Ni distance in the column, is decreased, while the packing distance of the column expands as illustrated in Fig. 9. The decrease in the intermolecular distance causes the discontinuities of the column while the expansion of the column distances should squeeze surrounding molecules out of their original positions when the change in lattice dimensions takes place inside the crystal. Such a situation can be observed in Fig. 15 which is the electron micrograph of the reaction intermediate. Part *A* remains unchanged showing the lattice distance of 13 Å whereas in the other part *B* the 14 Å lattice fringes can be observed with some discontinuities and bending. From these observations the molecular



(*a*) (*b*)

Fig. 14. A schematic representation of the structural change due to iodine-doping. (*a*) Original Ni(phc) and (*b*) complex with iodine.

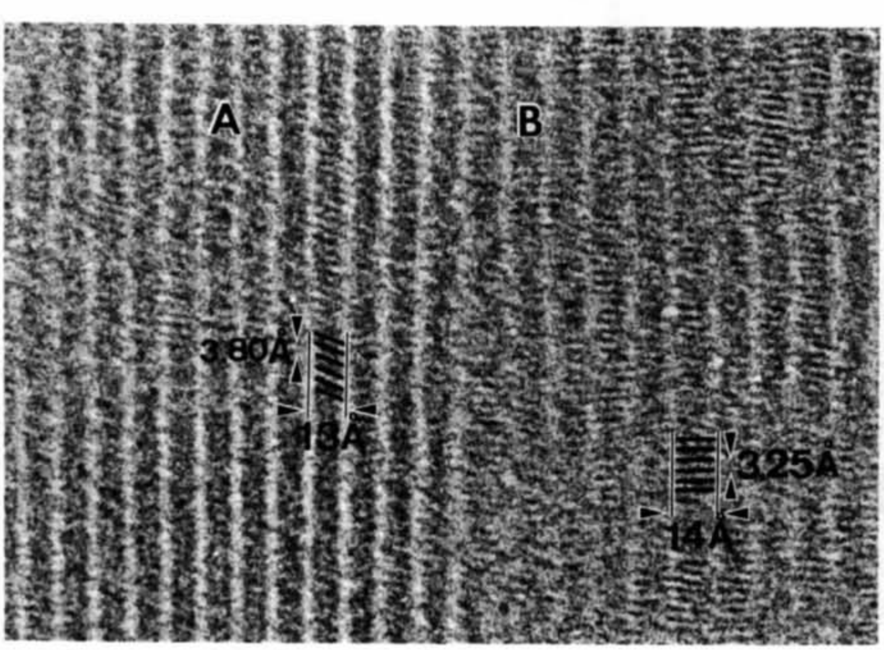


Fig. 15. High-resolution molecular images in the reaction intermediates.

rearrangement does not seem to take place in the manner of falling dominoes in a molecular column. The present work proves that the doping of iodine into a crystal of Ni(phc) occurs from several parts of the film.

The topotactic reaction model has also been confirmed by this investigation. The axial correlation between the matrix and the complex crystals has been revealed from the diffraction pattern of the reaction intermediate which is a nonstoichiometric complex of Ni(phc).$I_x$ ($x < 1{\cdot}0$), *i.e.* an iodine-doped crystal. With the crystal of Ni(phc) with the *b* axis parallel to the substrate such as mica, the electron diffraction pattern including the *b* axis and *c* axis of each crystal can be obtained (Fig. 5*b*), showing that the direction of the molecular columns of the complex crystal coincides with that of the original, though a slight deviation or disorder is introduced. On the other hand, the diffraction pattern from the crystal doped with iodine on KCl has shown that the direction of the molecular column has changed during the complex formation (Fig. 14*b*). Although the molecular column in the crystal on KCl stands obliquely against the substrate face before the reaction, the column in the complex which is parallel to the *c* axis has become perpendicular to the substrate as deduced from the electron diffraction and, more obviously, from high-resolution electron micrographs. This difference in these two cases can be interpreted as follows. The doping reaction takes place also from the surface of the dendrite crystal of Ni(phc) grown on KCl in which the molecular columns stand nearly perpendicularly to the substrate. However, the bottom molecules facing the substrate must have a strong interaction with the substrate ions through which the epitaxial growth has been originated. This interaction has remained unchanged even when the iodine doping has taken place as far as the adsorbed molecules and the substrate ions are concerned. Therefore, the molecular column newly formed by doping directly onto KCl should stand normal on top of the bottom molecules. In other words, the adsorbed molecules on the KCl surface define the direction of the axes of the molecular columns, and subsequently the crystal main axis, in the case of topotactic growth through solid-vapor reaction as well as in the case of the epitaxial growth on KCl from the vapor phase.

In order to prove that the strongly adsorbed molecule on the substrate acts as a nucleus of a complex crystal grown through the solid–vapor reaction, the substrate was obliterated before the doping reaction. The epitaxial film of Ni(phc) on KCl was reinforced with a thin carbon film, stripped off the substrate, fixed on a microgrid and then brought into contact with iodine vapor. It reacted partly after an hour. The resulting crystallites assume the same morphology as the product obtained on KCl previously shown in Fig. 12(*a*). However, the electron diffraction pattern (Fig. 16*b*) was an oblique pattern where both diffractions from the matrix Ni(phc) and the complex coexist. The pattern shows that the *c* axis of the iodine complex and the *b* axis of the matrix are tilted from the normal of the substrate with the same angle. This fact agrees with the above-mentioned results that the molecular column of the complex has become parallel to that of the matrix when the complex formation takes place on a mica substrate. The interaction force between mica and the Ni(phc) molecule is not so strong under the growth conditions of Ni(phc) adopted here.

The stacking of Ni(phc) in the iodine complex has been given by Schramm *et al.* (1980) as shown in Fig. 17. The molecules stack parallel forming the

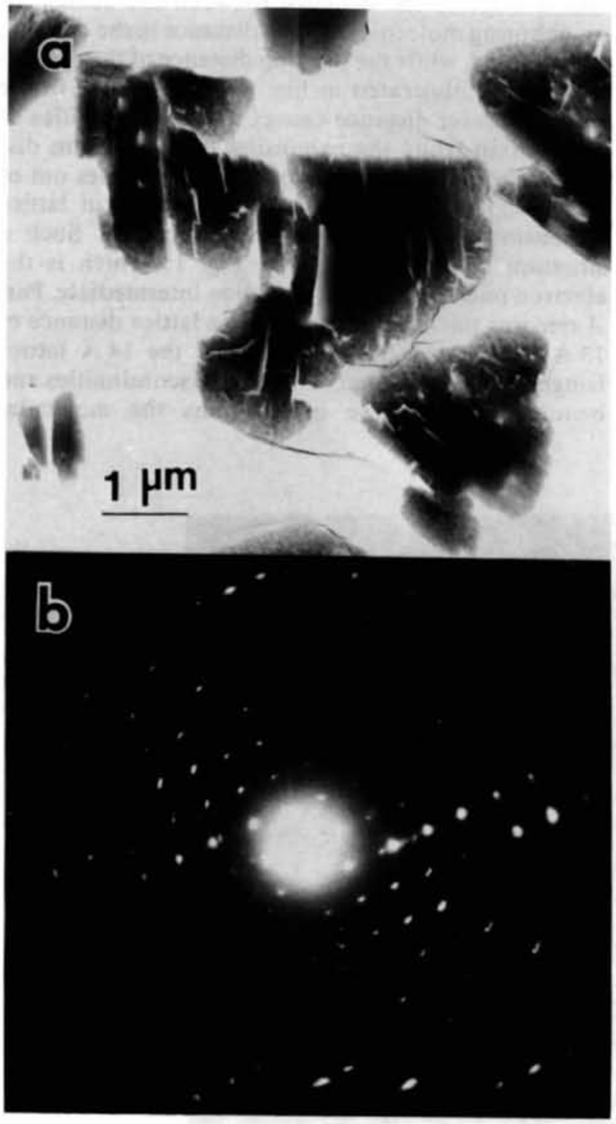


Fig. 16. (*a*) Electron micrograph and (*b*) selected-area diffraction pattern of Ni(phc) reacted with iodine on carbon film.

molecular column but are staggered alternately with an angle of 39·5°. Iodine is placed at every corner of the unit cell. In the electron micrographs presented here, no distinct image of iodine was detected. This may be due to the uncertainty of the iodine positions in a nonstoichiometric complex, such as the case studied here. The determination of the iodine position in such specimens will be made in future with a thinner specimen mounted on a low-temperature stage of an electron microscope suitable for high-resolution work. The present investigation has revealed that a small amount of doping can cause the structure change in the matrix crystal and that many disorders are introduced in the crystal. At the same time, the direct observation of molecular images by high-resolution electron microscopy has proved the possibility of the determination of molecular arrangements in reaction intermediates of organic crystals.

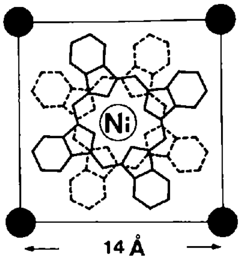


Fig. 17. A schematic representation of the crystal structure of Ni(phc).I$_{1.0}$ after Schramm *et al.* (1980).

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# Characterizations of the Monohydrates of the Monosodium and Dipotassium Salts of *cis–syn* Thymine Photodimer.* Crystallographic Treatments of Mixed Crystals Containing Dimers and Monomers Resulting from X-ray Cleavage of Dimers in the Solid State†‡

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## Abstract

The monohydrated monosodium and dipotassium salts of *cis–syn* thymine photodimer, $Na^+.C_{10}H_{11}N_4O_4^-.H_2O$ and $2K^+.C_{10}H_{10}N_4O_4^{2-}.H_2O$, have been prepared and their structures unambiguously determined by X-ray analyses. The sodium salt ($M_r = 292{\cdot}233$) crystallizes in the monoclinic space group $P2_1/n$ with $a = 6{\cdot}555\,(1)$, $b = 29{\cdot}010\,(3)$, $c = 6{\cdot}762\,(1)$ Å, $\beta = 106{\cdot}028\,(6)°$, $V = 1235{\cdot}88$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}570$, $D_m = 1{\cdot}53$ g cm$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·5418 Å, $\mu$(Cu $K\alpha$) = 13·925 cm$^{-1}$, $F(000) = 608$, $T = 297$ K. The successful analysis of the structure was accomplished [final $R(F) = 0{\cdot}051$] with the assumption that the crystal consists of the dimers intermingled with the monomer products of their X-ray cleavage and that the gradual photomonomerization takes place as a linear function of exposure. The results of the analysis, in which monomers were treated as rigid groups, revealed

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[*] Sodium hydrogen 4a,4b-dimethyl-4a,4b,8a,8b-tetrahydrocyclobuta[1,2-*e*:3,4-*e*′]dipyrimidinate monohydrate and dipotassium 4a,4b-dimethyl-4a,4b,8a,8b-tetrahydrocyclobuta[1,2-*e*:3,4-*e*′]dipyrimidinate monohydrate.

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