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The Orientation Overgrowth of Polycyclic Aromatic Quinones on the Cleavage Surface of Alkali Halide Single Crystals

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Vacuum-condensed films of polycyclic aromatic quinones (flavanthrone, indanthrone, and pyranthrone) were found to grow epitaxially on the cleavage faces of NaCl and KCl. Electron microscopy studies have shown that all the films on NaCl were composed of small, needle-like crystallites crossing orthogonally. The needle axis of the crystals coincides with the ⟨110⟩ directions of NaCl. When a cleavage surface of KCl was used as the substrate, vacuum-condensed films of flavanthrone and indanthrone were composed of dendroid crystals which assumed the standing *b*-axis orientation with an apparent C_{4v} symmetry. On the other hand, a pyranthrone film on KCl was composed of wedge-like crystals which assumed the standing *b*-axis orientation. The electron-diffraction pattern of the film revealed that the *b*-axis of each crystal tilts against the normal of the substrate face at an angle of 29° and takes a random orientation. When the films assume the standing *b*-axis orientation, the planar molecule in the crystal comes into parallel contact with the cleavage face of KCl. It may be presumed that the nitrogen atoms in both flavanthrone and indanthrone molecules are placed on potassium ions in the (001) plane of KCl.

The epitaxial crystallization of organic compounds on a cleavage face of alkali halides has been observed by many investigators. The orientation overgrowth of polyethylene,[1,2] *p*-aminobenzoic acid and sulfonicamide,[3] polyethylene and various other polymers,[4,5] poly γ-benzyl L-glutamate[6] and five oligopeptides[7] has been reported in little more than a decade. In these experiments, epitaxial deposits were formed on alkali halide surfaces from a supersaturated solution of the crystallizing substances.

In a previous paper, condensed polycyclic aromatic compounds were found to grow epitaxially when they

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[1] J. Willems, *Discuss. Faraday Soc.*, **25**, 111 (1957).

[2] E. W. Fischer, *ibid.*, **25**, 204 (1957).

[3] H. Seifert and L. Kuhn, *Naturwissenschaften*, **49**, 537 (1962).

[4] J. A. Koutsky, A. G. Walton, and E. Baer, *J. Polym. Sci., Part A-2*, **4**, 611 (1966).

[5] J. A. Koutsky, A. G. Walton, and E. Bare, *Polym. Lett.*, **5**, 177 (1967).

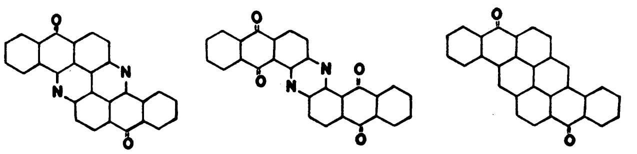
[6] S. H. Carr, A. G. Walton, and E. Baer, *Biopolymers*, **6**, 469 (1968).

[7] S. H. Carr and W. C. Colket, *J. Colloid Interfac. Sci.*, **31**, 328 (1969).

were condensed onto a cleavage face of a muscovite crystal *in vacuo*.[8] These molecules consist largely of flat benzene rings. In the crystals they are stacked together to form a column, in which the molecules are parallel to one another. The normal of the molecular plane is slightly tilted against the column axis. Thin films of copper-phthalocyanine, one of polycyclic aromatic compounds, when vacuum-sublimated on muscovite had two sorts of orientation according to the conditions of sublimation.[9,10] Similarly, phthalocyanine crystals deposited on a cleavage face of alkali halides took two types of orientation in compliance with the sort of substrate crystal.[11] These two orientations were called the parallel *b*-axis and the standing *b*-axis orientation, according to the direction of the *b*-axis of the crystal relative to the substrate face. In the crystal with the parallel *b*-axis orientation, the flat molecule stands obliquely on the substrate face and touches it at several points. On the contrary, in the case of the standing *b*-axis orientation the molecular planes are in contact parallel to the substrate face and the apparent symmetry of the oriented crystals is determined by the molecular symmetry. The basic orientation taken by a single molecule is determined by the molecular interaction between substrate atoms and adsorbed gas on the cleavage face. The molecules of polycyclic aromatic quinones have lower symmetry than that of phthalocyanine, and their way of packing in the crystal is remarkably similar to that of the latter. In order to establish that two such kinds of orientation occur also for other condensed polycyclic aromatic compounds, similar polycyclic aromatic quinones were vacuum-sublimated onto a cleavage face of alkali halides and the orientation overgrowth of these crystals was investigated by means of electron microscopy as well as by means of electron diffraction.

Experimental

The polycyclic aromatic quinones used in this work were flavanthrone ($C_{28}H_{12}O_2N_2$), indanthrone ($C_{28}H_{14}O_4N_2$), and pyranthrone ($C_{30}H_{14}O_2$); their constitutional formulas are shown in Fig. 1. These compounds were purified by repeated sublimation in a low-pressure stream of carbon dioxide at a temperature above 400°C and were examined by means of an X-ray diffractometer. The purified materials were sublimated from a tungsten basket onto a clean surface of alkali halide in a vacuum evaporator, as has been described in a previous paper.[10] Single crystals of rock salt and sylvine were used as the substrate. They were cleaved in air and immediately placed in the vacuum evaporator. The temperature of the substrate was kept in the range from 100 to 200°C.



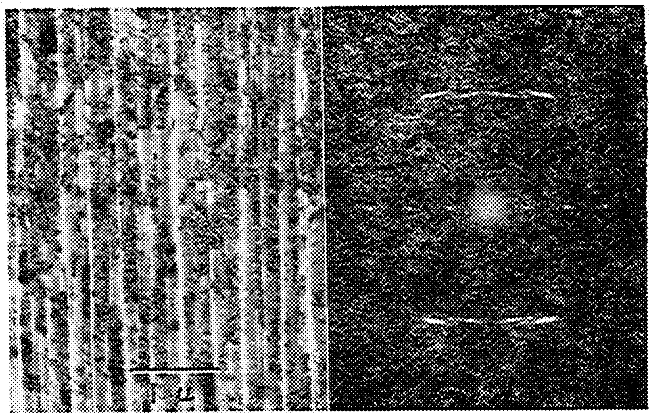
Flavanthrone Indanthrone Pyranthrone

Fig. 1. Constitutional formulas of quinones.

The specimens used for electron microscopy were prepared by the wet-stripping method after they had been reinforced with evaporated carbon film. Thallium chloride prepared by deposition *in vacuo* was used as a standard calibration material for the spacing measurements.

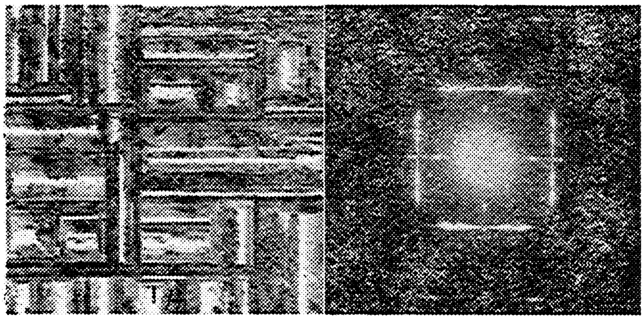
Results

A) Epitaxial Growth on Rock Salt. When flavanthrone was sublimated onto a cleavage face of rock salt at 150°C, certain areas of the film showed the well-defined, sngle-directional orientation whose electron micrograph and electron-diffraction pattern are shown in Figs. 2(a) and (b) respectively. The film was composed of laminar crystal strips giving rise to a raft structure as a whole. The fiber diagram obtained from the film reveals that the meridian coincides with the needle axis of the crystal strips. The maximum lattice spacing along this direction turned out to be 3.81 Å, which is in good agreement with the unit cell length of the *b*-axis. The diffraction spots on the equator have an equidistance of 8.10Å, which



(a) (b)

Fig. 2. Electron micrograph (a) and electron diffraction pattern (b) of flavanthrone film vacuum-condensed onto the (001) plane of NaCl. Crystals assume the parallel *b*-axis orientation with single direction.



(a) (b)

Fig. 3. Electron micrograph (a) and electron diffraction pattern (b) of flavanthrone film vacuum-condensed onto the (001) plane of NaCl. Crystals assume the parallel *b*-axis orientation with double direction.

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[8] E. Suito, N. Uyeda, and M. Ashida, *Nature*, **194**, 273 (1962).

[9] N. Uyeda, M. Ashida, and E. Suito, *J. Appl. Phys.*, **36**, 1453 (1965).

[10] M. Ashida, This Bulletin, **39**, 2625 (1966).

[11] M. Ashida, *ibid.*, **39**, 2632 (1966).

corresponds to 001 and its higher-order reflections. Thus, each crystal strip grows along the *b*-axis and its (001) plane lies parallel to the substrate face. The other areas of the flavanthrone film were composed of two groups of slender crystal strips crossing each other orthogonally, as is shown in Fig. 3 (a). Corresponding to such a configuration of the film, the diffraction pattern also had an orthogonal appearance, as Fig. 3(b) shows. This pattern is a superposition of two identical fiber diagrams, each of which is essentially the same as that of the single-directional orientation mentioned above. In order to establish the orientation of the deposited crystals relative to the substrate rock salt, well-developed crystals on the cleavage face were observed by means of an optical microscope. The needle axis of the deposited crystals was found to be parallel to the <110> direction of the substrate crystal.

When indanthrone was sublimated onto a cleavage face of rock salt, the film was built up of quite the same networks of laminar crystal strips crossing orthogonally as those of flavanthrone film. The electron-diffraction pattern in Fig. 4(a) also shows that the film assumes a double-directional orientation with strips crossing each other rectangularly. Each fiber spacing with a distance of 3.83 Å coincides with the unit length of the *b*-axis, and the series of the spots on the equator with a interplanar spacing of 15.4 Å corresponds to 200 and its higher-order reflections. The individual *b*-axis of the crystal was parallel to the <110> direction of rock salt.

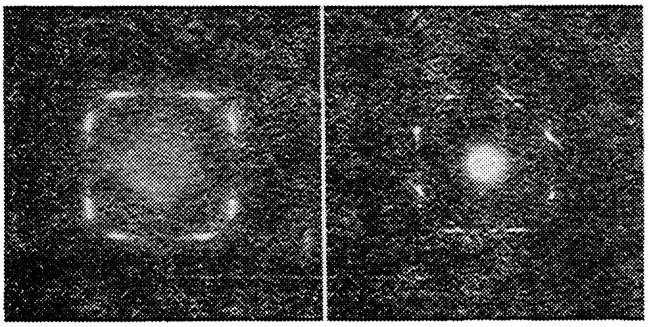

(a) (b)

Fig. 4. (a): Electron diffraction pattern of indanthrone film vacuum-condensed onto the (001) plane of NaCl at 150°C. (b): Electron diffraction pattern of pyranthrone film vacuum-condensed onto the (001) plane of NaCl at 200°C.

Pyranthrone films sublimated on rock salt took the same double-directional orientation as flavanthrone and indanthrone when the substrate was held to under 150°C. On the other hand, a triple-directional orientation was observed when the temperature of the substrate was raised to 200°C. An electron-diffraction pattern of the resulting film is a superposition of three identical fiber diagrams, as is shown in Fig. 4(b). The two dominant directions coincide with both the [110] and [1$\bar{1}$0] directions of rock salt, while the other faint direction runs parallel to the [100] direction of the substrate crystal. It should be noted that there are a few crystallites of pyranthrone growing along the [100] direction of the substrate rock salt as the temperature is raised to 200°C.

The characteristic behavior of the crystals deposited on rock salt is that their *b*-axes run parallel to the substrate face and that, consequently, they assume the parallel *b*-axis orientation.

B) Epitaxial Growth on Sylvine. When a cleavage face of sylvine was used as the substrate, vacuum-condensed films of polycyclic aromatic quinones showed quite a different orientation from those on the rock salt.

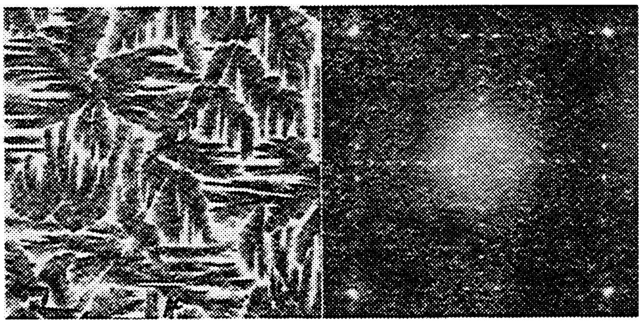

(a) (b)

Fig. 5. Electron micrograph (a) and electron diffraction pattern (b) of flavanthrone film vacuum-condensed onto the (001) plane of KCl. Crystals assume the standing *b*-axis orientation.

Flavanthrone crystals sublimated onto sylvine grow well-defined dendrites and form a discrete film, as is shown in Fig. 5(a). The electron-diffraction pattern of the film shown in Fig. 5(b) appears to overlap two single crystal patterns crossing orthogonally each other in spite of the reflections from many crystallites. This finding suggests that all the crystals deposited on sylvine take a well-defined orientation. Since the series of spots on the equator is equidistant corresponding to the interplanar spacing of 13.9 Å, they are clearly 200 and its higher-order reflections. On the contrary, the spacing of 1.75 Å, which is obtained from the distance between the first layer line and the equator, does not agree with any unit length of the crystallographic axes. The appearance of such layered lines should be ascribed to the position of the main zone axes of the deposited crystals, which are tilted against the substrate face and, consequently, against the electron beam. Because the equatorial spots have the indices of $h00$, all the spots within each layer line should have indices with the same k and l values. The spacing of the (014) plane is 1.78 Å. Thus, the spots on the layer lines above and below the equator correspond to $h14$ (or $h1\bar{4}$) and $h\bar{1}\bar{4}$ (or $h\bar{1}4$) respectively, and the *b*-axis of the crystal makes an angle of about 28° with the normal of the substrate face. The diffraction spots were indexed as is shown schematically in Fig. 6, in which the white circles represent the basic single crystal pattern. The total pattern is obtained by a superposition of this elementary pattern by the symmetry operation of C_{4v}, whose major axes are XX′ and YY′. By relating the orientation to the substrate crystal, the *a*-axis of flavanthrone was found to run along the <110> direction of sylvine.

In the case of indanthrone, the deposited film on

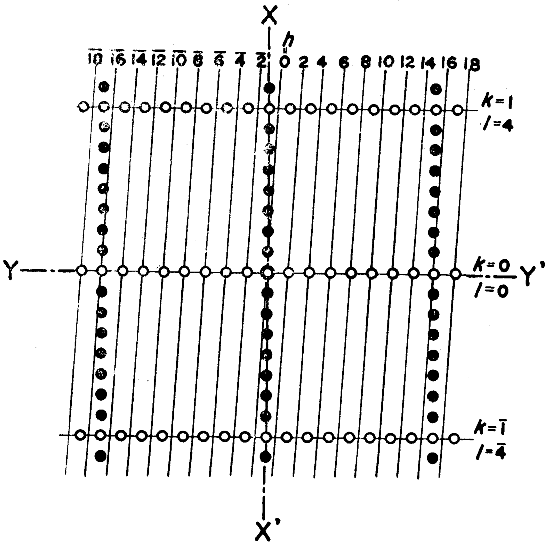


Fig. 6. The interpretation of the diffraction pattern shown in Fig. 5. White circles are the representation of the basic single pattern.

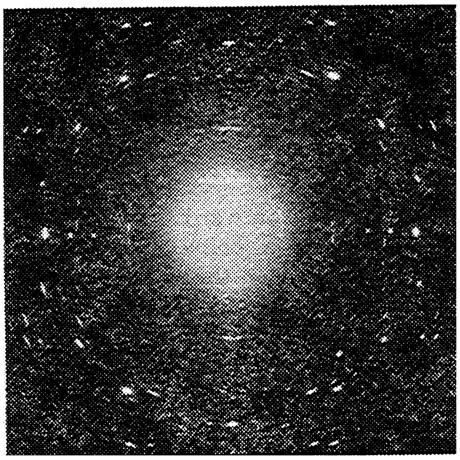


Fig. 7. Electron diffraction pattern of indanthrone film vacuum-condensed onto the (001) plane of KCl.

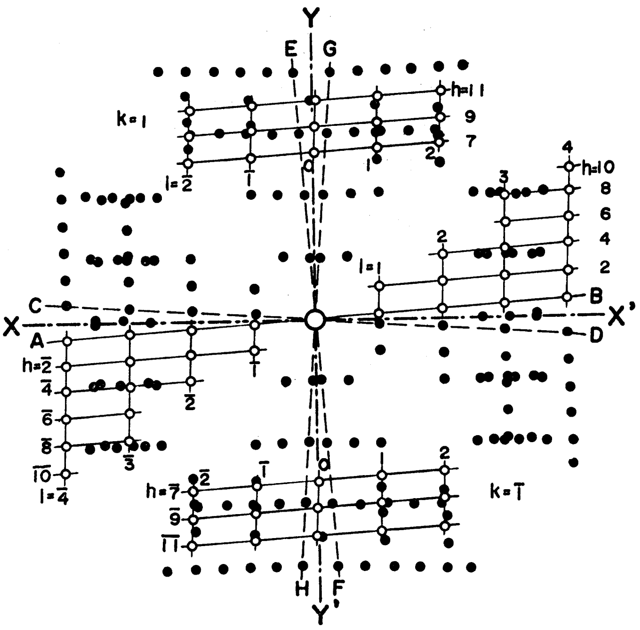
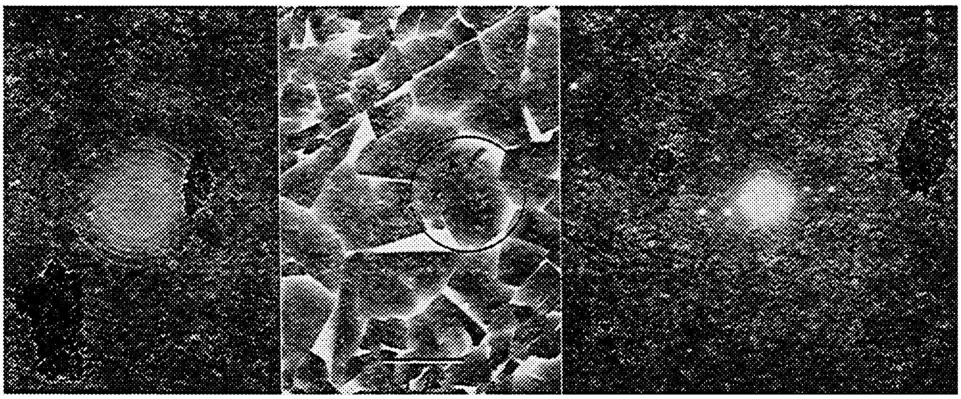


Fig. 8. The interpretation of the diffraction pattern shown in Fig. 7. White circles are the representation of the basic single crystal pattern.

sylvine was composed of dendroid crystals similar to those of flavanthrone. The electron-diffraction pattern of the film shows a complicated pattern with the C_{4v} symmetry, as is represented in Fig. 7. Therefore, the film turned out to include eight groups of crystals, in each of which the crystals had the same orientation. Each elementary cross-grating pattern consits of three parallel regions. The unit length of the b-axis is more shorter than those of the a- and c-axes, so the reciprocal lattice plane with $k=1$ is located at a far distance compared with the other reciprocal lattice planes. Therefore, the spots in the region which includes the origin are the $h0l$ reflections. They appear as at the intersection of the reciprocal lattice points as well as in their elongated intensity regions with the Ewald sphere. The other regions, which do not pass through the point of origin, correspond to the reciprocal lattice planes of $k=\pm 1$. Thus, the total diffraction pattern is as is schematically reproduced in Fig. 8, in which the white circles indicate the basic single crystal pattern associated with one of two groups of crystals which have an apparent C_2 symmetry. Although the total pattern appears to be complicated, it can be illustrated by the systematic superposition of this elementary pattern with the major axes of C_{4v} symmetry, XX' and YY', which further coincide with the [110] and $[1\bar{1}0]$ directions of sylvine respectively. From a consideration of the observed and calculated spacings as well as the intensities, the reciprocal lattice points, 804 and $91\bar{2}$, were found to lie directly on the Ewald sphere. Consequently, the a-, b-, and c-axes of the crystal are inclined to the normal of the substrate face at angles of about 120°, 35°, and 76° respectively. As the AB line is the reciprocal c^* axis in the elementary pattern, the other lines, CD, EF, and GH, are similar c^* axes associated with individual crystal groups. Each reciprocal c^* axis was found to make an angle of about 5° with the nearest major axis of C_{4v} symmetry.

Well-developed crystals of pyranthrone sublimated on sylvine had a definite wedge-like form, as is shown in Fig. 9(a). The electron-diffraction pattern of Fig. 9(b) represents an imperfect ring diagram, which indicates a random orientation. However, a selected area electron-diffraction pattern from one of the crystals, such as the one circled in Fig. 9(a), gave a single net pattern composed of three separate regions, as Fig. 9(c) shows. The diffraction spots were indexed as is schematically shown in Fig. 10. Considering the interplanar spacings and the intensities of the diffraction spots, it is found that the reciprocal lattice points, 105 and $10,1,\bar{3}$, lie directly on the Ewald sphere. Consequently, the b-axis of the crystal tilts against the normal of the substrate surface at an angle of about 29°. If this single net pattern rotates around the point of origin, the resulting diagram coincides with the ring pattern of Fig. 9(b). Therefore, the random orientation seen in Fig. 9(b) arises from the differences in the tilting directions of the b-axes of the individual



(b) (a) (c)

Fig. 9. Electron micrograph (a) and electron diffraction pattern (b) of pyranthrone film vacuum-condensed onto the (001) plane of KCl. Selected area diffraction pattern (c) of the crystal indicated by the circle in (a).

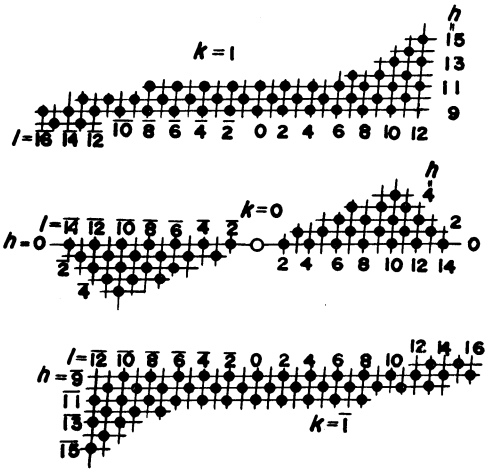


Fig. 10. The interpretation of the diffraction pattern shown in Fig. 9 (c).

crystallites, though the inclination angle of each *b*-axis to the normal of the substrate face is always a constant value of 29°.

Discussion

The crystal data of indanthrone, flavanthrone, and pyranthrone reported by Bailey,[12] Stadler,[13] and Maitland and Stadler[14] are summarized in Table 1. The molecules of polycyclic aromatic quinones are composed of many condensed benzene rings and form a flat plane, or a nearly flat one, as a whole. These flat molecules are closely packed together in a column, giving rise to a tilt against the column axis. The inclination angles of the molecular plane against the orthogonal *a*-, *b*-, or *c**-axis of each crystal are also shown in Table 1. When flavanthrone was sublimated on rock salt, the (001) face of the deposited crystal lay parallel to the substrate surface and its *b*-axis ran along either the [110] or [1$\bar{1}$0] axis of the substrate crystal. Since the planar molecules are not parallel to the (001) plane, they stand obliquely on the substrate surface so that they come in contact with the interface at several points. It is a problem which ion of sodium chloride attracts the deposited molecule and which atom of the flavanthrone molecule touches the substrate face. However, if a particular part in one molecule is located on the top of one Na^+ or Cl^- ion, it is likely that the same part of the adjacent molecule along the *b*-axis comes near to the top of the other like-charged ion and the crystal grows along the *b*-axis to form rod-like outward. In the cleavage face of rock salt, the distance between like-charged ions is 5.63 Å and 3.97 Å along the [100] and [110] axes respectively. Comparing these values with the length of the *b*-axis of the flavanthrone crystal, it seems reasonable that the preferential orientation of the deposits in the <110> directions occurs in the cleavage face of rock salt. The same characteristic behavior of other quinones, indanthrone, and pyranthrone was found in their epitaxial growth on rock salt. When the strips assume a cross-directional raft structure, the mutual orientation is uniquely defined and the needle axis of individual strips, essentially the *b*-axis, coincides with the <110> directions of rock salt. In the case of pyranthrone, in addition to these directions, a small number of crystallites oriented their *b*-axis parallel to the [100] direction of rock salt at high temperatures above 200°C. The different orientation observed in the pyranthrone film may be due to a weaker interaction between the deposit and substrate ions than those in the other quinones studied. If the energy of thermal vibration is not very high, the orientation in the <110> direction caused by this interaction will be favored. If the substrate temperature is raised and the energy of thermal vibration becomes high, the effect of the interaction will be reduced relatively and the alignment of the crystal will not be entirely specific in the <110> directions. Recently, Koutsky *et al.*[4,5] have reported that some polymers which crystallized epitaxially from a solution on alkali halide surfaces grew small, rod-like crystallites with an orientation in the <110> directions of the substrates. They also concluded that the polymer epitaxy was dependent on rows of like-charged ions in the

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[12] M. Bailey, *Acta Crystallogr.*, **8**, 182 (1955).

[13] H. P. Stadler, *ibid.*, **6**, 540 (1953).

Table 1. Crystal data of quinones

		Flavanthrone	Indanthrone	Pyranthrone
Unit cell constants	a (Å)	27.9	30.8	22.0
	b (Å)	3.80	3.83	3.84
	c (Å)	8.10	7.84	21.2
	β	95°	92°	90°
	z	2	2	4
Space group		$P2_1/a$	$P2_1/a$	$P2_1/n$
Angles between crystal axes and the normal of molecular plane				
	a-axis	105°, 75°	110°, 80°	
	b-axis	26°	26°	26°
	c^*-axis	72°, 108°	75°, 105°	

substrate surfaces.

On the contrary, when sylvine was used as the substrate, the deposited films showed quite a different orientation, one giving rise to various morphological features. In the case of the flavanthrone crystal on sylvine, its b-axis is inclined to the normal of the substrate face at an angle of 28° and the a-axis runs along the <110> directions of sylvine. Because the molecular plane of flavanthrone is inclined against the (010) plane at an angle of 26°, the standing b-axis orientation suggests that the planar molecule nearly comes in contact parallelly with the substrate face. In heterocyclic compounds the charge is distributed on nitrogen atoms with a high density.[15] Therefore, in the planar molecule facing the substrate, it seems reasonable to assume that the nitrogen atoms of the molecule come in contact with K^+ ions, as is schematically shown in Fig. 11. A projection of the above molecules facing parallel along the b-axis on a molecular plane shifts in either the b_p or b_p' direction, which coincides with the [110] direction of sylvine, depending upon the staggering of the overlapping molecule. This configuration results in two different crystals which are related by a two-fold rotation axis. As sylvine has a four-fold rotation axis perpendicular to its (001) plane, the same relative orientation between the deposited and substrate crystals is obtained by the rotation of 90° in the deposited molecule. This gives rise to two different crystals, the projection of whose b-axis coincides with the $[1\bar{1}0]$ direction of sylvine. Thus, the total film consists of four groups of oriented crystals and the electron-diffraction pattern from them gives two overlapping diagrams crossing orthogonally. However, when we compare the inclination angles of the crystal axes to molecular plane with the tilting angle of the oriented crystal, it is clear that the flat molecule does not lie strictly parallel to the substrate face. Presumably each molecule is initially adsorbed parallelly to the (001) plane of sylvine, but the intermolecular force among neighboring molecules pulls the lying molecule slightly up, so that a perfect three-dimensional configuration builds up within the crystal.

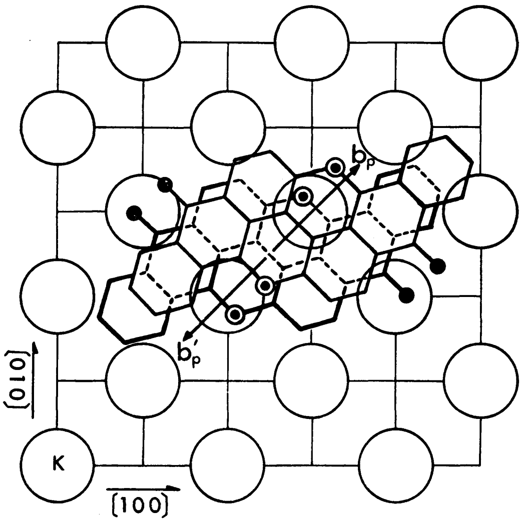

Fig. 11. The lattice structure of the (001) plane of KCl and the relative orientation of the deposited flavanthrone.
●: oxygen atom
⊙: nitrogen atom

The crystal of indanthrone sublimated on sylvine took the standing b-axis orientation, in which the a-, b-, and c-axes are inclined to the normal of the substrate face at angles of about 120°, 35°, and 76° respectively. When we compare these values with the inclination angles of the molecular plane against the crystal axes, it seems reasonable to conclude that the molecular plane comes into parallel contact with the substrate face. If the nitrogen atoms of the molecule are assumed to lie on K^+ ions, as is schematically shown in Fig. 12, a projection of the above molecule facing parallel along the b-axis on a molecular plane shifts in either the b_p or b_p' direction, which makes an angle of 30° with the $[1\bar{1}0]$ direction of sylvine. A projection of the c-axis on a molecular plane makes an angle of 125° with that of the b-axis, as is shown by the OA and OB lines concerned with b_p and b_p' and, consequently, makes an angle of 5° with the [110] direction of sylvine; this results in two different crystals related by the two-fold rotation axis. It should be noted that this angle coincides with that between the projection of the reciprocal c^*-axis of the indanthrone crystal and the [110] direction of sylvine as revealed by the electron-diffraction pattern. If a molecule is rotated about the XX' axis by 180°, the molecule lies at the same position relative to the substrate ions. In this case, a projection

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[15] H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).

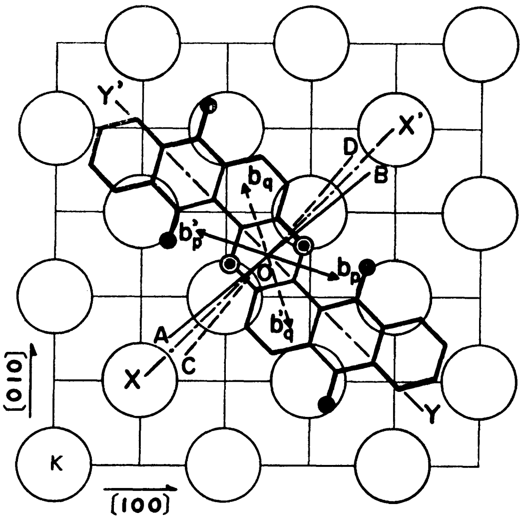

Fig. 12. Schematic diagram of the relative orientation of indanthrone to the (001) plane of KCl.
●: oxygen atom
⊙: nitrogen atom

of the *b*-axis on the surface makes an angle of 30° with the $[1\bar{1}0]$ direction of sylvine, as is shown by b_q and b_q', and the projection of the *c*-axis is as is represented by the CD line. Consequently, such a molecular orientation gives rise to four sets of crystals with an apparent C_{2v} symmetry, whose mirror plane is perpendicular to the [110] direction, as is represented by the XX′ line. Moreover, the same relative orientation between the deposited and substrate crystals is obtained by the rotation of 90° in the deposited molecule. The orientation of the resulting crystals has a symmetry of C_{2v} as a whole, whose mirror plane is perpendicular to the $[1\bar{1}0]$ direction, as is represented by the YY′ line. Thus, the total film involves eight sets of oriented crystals and shows an apparent C_{4v} symmetry, as far as the orientation of individual crystallites is concerned.

In the pyranthrone film vacuum-sublimated on sylvine, the individual crystals assumed the standing *b*-axis orientation, in which the *b*-axis tilted against the substrate face with an angle of 29°. However, the ring pattern from the total film suggested that the individual tilting *b*-axis took a random direction independent of the alignment of ions in the cleavage face of sylvine. When the inclination of the molecular plane to the crystal axes is considered, it is clear that the molecular plane is parallel to the substrate face, but no strictly preferential location of the component atoms in the deposited molecule seems to occur in this case. Pyranthrone is closely related to flavanthrone, in which the two C-H groups are replaced by N atoms. Both flavanthrone and indanthrone belong to the same structure type with the $P2_1/a$ space group, and their molecular planes are tilted about the C–O bond as an axis. On the other hand, pyranthrone belongs to a different structure type which contains two independent molecules per asymmetric unit. Perhaps there is a difference in the intermolecular forces of pyranthrone and the other quinones studied.

The various orientations on the cleavage faces of alkali halides may be caused by the complex combination of mutual interaction between the deposited and substrate crystals and the intermolecular force within the crystal. The condensed polycyclic aromatic compounds include π electrons out of the molecular plane. These electrons may affect the way of molecular adsorption by interaction with the gas which is adsorbed on the substrate face in advance, as been described in previous papers.[10,16] Therefore, the mode of molecular adsorption, the parallel *b*-axis or the standing *b*-axis orientation, is perhaps primarily determined by the interaction between these π electrons and the substrate face. The position of the individual component atoms relative to the substrate ions is determined by the charge distribution in the molecule itself. The influence of adsorption gas on orientation overgrowth will be described in a future report. For organic crystals composed of large flat molecules, we may suppose that both the charge distribution and the configuration of the molecules themselves, as well as the total lattice dimensions of the deposited and substrate crystals, are important in determining epitaxial growth.

The authors wish to thank Professor Eiji Suito and Dr. Natsu Uyeda of the Institute for Chemical Research, Kyoto University, for their many helpful discussions during this work.

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16) N. Uyeda, M. Ashida, and E. Suito, Sixth Intern'l Cong. Electron Microscopy, Kyoto, **1**, 485 (1966).