861. *Crystal Symmetry and the Adsorption of Dyes by Growing Crystals. Part II.* Potassium Nitrate.*

By JOHN WHETSTONE.

The suitability, for adsorption of dyes, of the principal low-index planes of potassium nitrate is discussed in the light of the scheme proposed previously by the author to explain modifications of crystal habit by dyes. Owing to the pseudohexagonal symmetry of the crystals about the axis normal to {001}, it is to be expected that dye adsorption will influence not only formation of pleochroic dye inclusions but also twinning tendencies. Evidence obtained by the study of modified crystals is consistent with the expectations.

THE ordinary-temperature modification of potassium nitrate crystallises in the orthorhombic system. In addition to single crystals, in which {110} and {010} are the only faces normally developed of the zone perpendicular to the basal plane {001}, pseudohexagonal " triplets " twinned on {110} can also crystallise. The earliest reference to the modification of crystal habit by dyes of potassium nitrate is by Retgers.[1] Instead of the usual long prisms, he obtained rounded tablets on {001} in the presence of soluble Nigrosine. This extension of the basal plane {001} has been confirmed to be the characteristic manifestation of " advanced " habit change of this salt with dyes. The crystals obtained may or may not contain pleochroic dye inclusions. They may be well-formed hexagonal {001} tablets, or aggregates of hexagons growing out from one another, lamellæ of very thin platy crystals with characteristic hexagonal outgrowths at the edges, platy crystals showing repeated pseudohexagonal twinning, or lath-like crystals showing occasional twinning rendered visible to the naked eye by virtue of closely crowded parallel striations which run lengthwise along the untwinned portions. The habit modification is very easily recognised by the centred " acute bisectrix " interference figures given by the crystals.

Other modifications of potassium nitrate are sometimes observed. For instance, occasionally platy or lath-like {010} crystals are produced, presumably by dye adsorption on forms of which *b* is the zone axis. Extremely acicular crystals are rarely encountered.

Examination of the Structure of Potassium Nitrate Crystals.—The *X*-ray structural determination employed in this study is that by Edwards.[2] The basal plane {001}, the plane usually developed in area by potent habit-modifiers, is structurally of low reticular density and consists of alternate layers of anions and cations separated by 1·05 Å. The nitrate ions are all coplanar and lying in {001}; so that for reasons given before,[3] the plane does not lend itself well to adsorption of planar sulphonated-dye molecules.

The principal planes perpendicular to {001} fall into two groups, the members of which are related by the pseudohexagonal symmetry of the crystal; {100} and {130} form one group. These forms are of high reticular density, and are composed of alternate rows of anions and cations (see Fig. 1). In {100} the rows are all coplanar, but in {130} the individual rows of anions are not exactly coplanar, two separate layers being formed about 1·07 Å apart. In many cases {100} and {130} may be expected to be equally suitable for dye adsorption; these forms would appear to be especially well adapted to the adsorption of planar dye molecules containing roughly equivalent numbers of anionic and cationic polar substituent groups.

{010} and {110} are the second group. The forms again are of high reticular density but are composed entirely of one kind of ion, planes of anions alternating with planes of cations in the crystal structure. In {010} the constituent ions of the plane are all coplanar

---

* Part I, *J.*, 1956, 4841.

[1] Retgers, *Z. phys. Chem.*, 1893, **12**, 582.

[2] Edwards, *Z. Krist.*, 1941, **80**, 154.

[3] Whetstone, *Trans. Faraday Soc.*, 1955, **51**, 973, 1142.

FIG. 1. *Fast-red E on potassium nitrate* {100}. *Single circles are* K *ions*; NO_3 *ions are in the plane perpendicular to the paper and are represented edgeways, the two* O *atoms and the* N *atom being shown.*

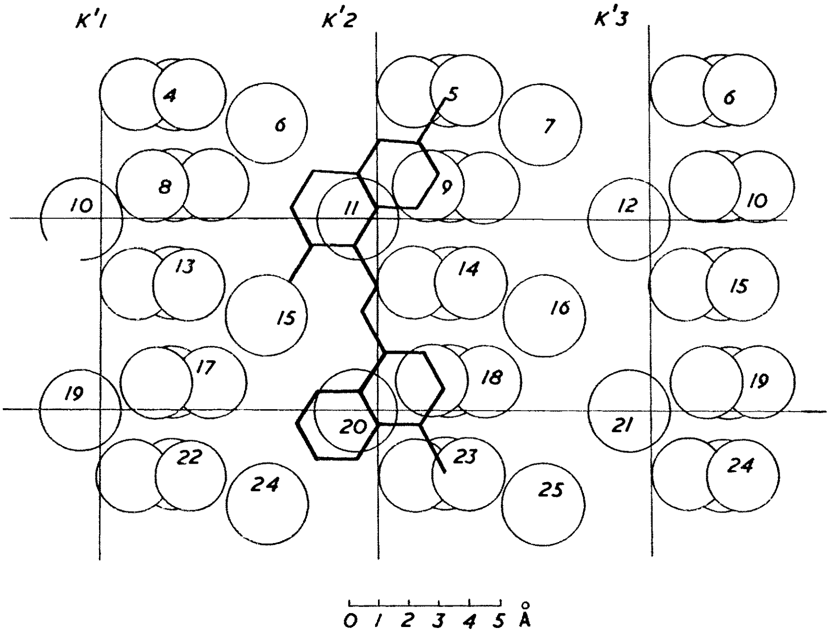
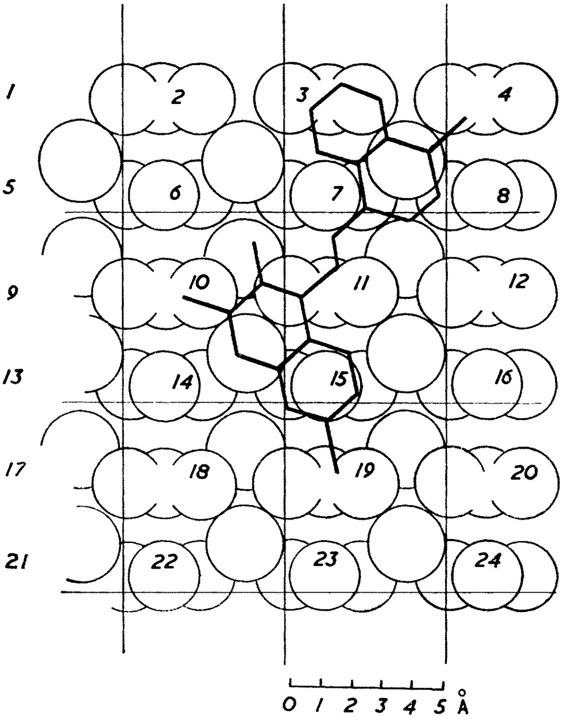


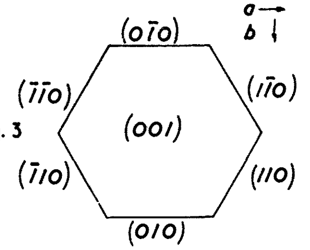
FIG. 2. *Amaranth on potassium nitrate* {010}. *Representation is as in Fig.* 1.



(Fig. 2) but again in {110} the alternate rows of anions lie in two layers separated by about 1·07 Å. In many cases both forms are likely to be equally suited to dye adsorption. The adsorption of dyes with a preponderance of one kind of polar substituent group is likely to be favoured on these planes.

Pleochroism of Modified Potassium Nitrate Crystals.—The similarities and the differences between {010} and {110}, and {100} and {130}, give a very wide scope for various modes of adsorption of different dyes. Various types of habit-modification behaviour are to be expected, depending on whether the resultant crystals are untwinned or pseudohexagonal triplets, and also which of the following planes are selected by the dye molecules for adsorption: (*a*) {010} alone, (*b*) {110} alone, (*c*) {110} and {010}, (*d*) {100} alone, (*e*) {130} alone, (*f*) {100} and {130}. Potassium nitrate is therefore likely to follow a more complicated pattern in its habit modifications than ammonium nitrate IV.[4] It is probable that some unusual effects observed with potassium nitrate may be due to the dye's being adsorbed simultaneously on planes with *b* and *c* respectively, their zone axes.

Fig. 3



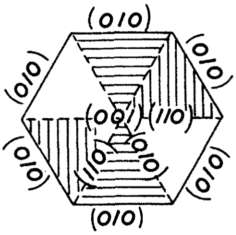
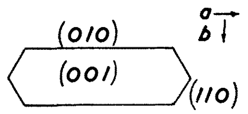


Fig. 4

Fig. 5



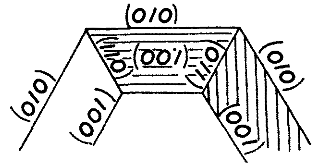


Fig. 6

FIG. 3. *Single crystal modified by adsorption on* {010}. *Growth on* {100} *and* {001} *most retarded. Crystal tends to be compact.*

FIG. 4. *Pseudohexagonal triplet modified by adsorption on* {010}. *Growth on* {100} *and* {001} *most retarded. Crystal tends to be hexagonal, owing to twinning on* {110}.

FIG. 5. *Simple crystal modified by adsorption on* {100}. *Growth on* {001} *and* {010} *most retarded. Crystal tends to be lath-like.*

FIG. 6. *Triplet modified by adsorption on* {100}. *Growth on* {100} *least retarded. Triplet shows characteristic elongation of sections, twinning being on* {110}.

If the dye molecules are adsorbed at once on more than one pinacoid of a pseudohexagonal crystal form, no pleochroism is likely to be observed, owing to the simultaneous interaction of the electric vector with electronic systems in different orientations. However, the structures of the pinacoids comprising the pseudohexagonal forms are not exactly similar, so that if the dye molecule is capable only of adsorption on one component pinacoid the modified crystals may contain pleochroic dye inclusions, in which case the detection of the plane of dye adsorption is facilitated.

The ordinary habit of potassium nitrate being somewhat elongated on {001}, it is apparent that to convert the normal crystals into the usual modified plates a great restraint must be imposed on the growth of {001}. Since this could conceivably be imposed by adsorption of dye on several alternative planes, it is instructive to predict the effects on crystal habit and pleochroism, assuming that growth is most affected on planes perpendicular to those on which the dye is adsorbed, and to compare experimental observations with the predictions (Table 1). Figs. 3—6 illustrate these effects.

---

[4] Whetstone, *J.*, 1956, 4841.

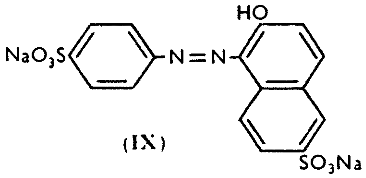
TABLE 1. *The effects of dye adsorptions on various planes on the nature of* {001} *modified crystals of potassium nitrate.*

Plane(s) of adsorption of dye	Predicted effects on modified crystals Single crystals	Triplets
{010} only	Should retard {100} and {001}. Strong pleochroism	Production encouraged owing to restriction of growth on *a*. Pleochroism in units of twins
{100} only	Should retard {010} and {001}. Strong pleochroism	The elongation on *a* should tend to suppress the formation of hexagonal triplets
{110} only	Pleochroism unlikely	No pleochroism
{010} and {110}	Flat hexagonal {001} plates. No pleochroism	No pleochroism
{130} only	Pleochroism unlikely	No pleochroism
{100} and {130}	Flat hexagonal {001} plates. No pleochroism	No pleochroism
Any other planes steeply inclined to {001}	No pleochroism, if planes multiplied by symmetry	No pleochroism
{001}	Pleochroism with unsymmetrical dye molecules only	Pleochroism with unsymmetrical dye molecules only

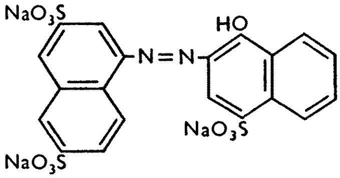
TABLE 2. *Potassium nitrate* {001} *modification: some crystal-habit modifying dyes.*

Structure *	Dye	Plane of adsorption (pleochroism)	Plane of adsorption (fitting)	Location of polar groups on diagram of plane (S = SO_3^- group)
I*d*	Fast-red E	{100}	{100}	S(4′)-23 OH(2)-15, S(6)-5
IX	—	{100}	{100}	S(4′)-23 OH(2)-15, S(6)-5
I*a*	Amaranth	{010}	{010}	S(4′)-4, S(3)-10, S(6)-19
I*b*	D.I.F.	—	{010}	S(4′)-4, S(3)-10, S(6)-19
I*e*	—	—	{010}	S(3′)-10, S(6′)-19, S(4)-4
X	—	—	{100}	OH-11, S(3′)-8, S(6′)-22 (near) S(4)-18
XI	Solochrome-yellow YS	—	{010}	S(6′)-22, S(8′)-14, CO_2H-7
VII*b*	Disulphonated Döbner's violet	—	{100}	(NH_2)*p*-2, (NH_2)*p*′-16, (S)*m*-5, (S)*m*′-18
XII	Ink-blue	—	{010}	S(*p*)-5, S(*p*′)-4, S(*p*″)-23
VIII	1 : 4-Diaminoanthraquinone-2-sulphonate	{100}	{100}	NH_2(1)-6, NH_2(4)-15, S-8
VIII*a*	Acid alizarin-blue	{010}	{010}	S(6)-15, S(2)-2

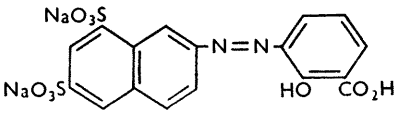
* Formula numbers are those of the earlier Part of the series (ref. 4), with the addition of [I*d*; 2-OH, 6 : 4-$(SO_3Na)_2$], [I*e*; 2-OH, 4 : 3′ : 6′-$(SO_3Na)_3$], [VIII*a*; 1 : 3 : 4 : 5 : 7 : 8-$(OH)_6$, 2 : 6; $(SO_3Na)_2$], (IX)—(XI) as annexed, and [(XII), tris-(*p*-sulphonated *N*-phenyl)pararosaniline (VI; R_2 = H, C_6H_4·SO_3Na-*p*)].



(IX)



(X)



(XI)

The observed pleochroic properties and habit of the modified crystals are usually consistent with the predictions in Table 1, and changes of habit may satisfactorily be explained by similarities between the orientations of polar groups of the dye molecules and the ionic structures of suitable crystal planes.

EXPERIMENTAL

Fast-red (AA) and Amaranth (BA), etc.—Fast-red E and amaranth differ in that the latter has an extra 3-sulphonate group. Whereas amaranth is generally quite a useful crystal-habit modifier, the activity of fast-red E is apparently specific to potassium nitrate. In spite of higher sulphonation, the habit-modifying power of amaranth, with apparently quite adequate solubility, is less than that of fast-red E and not quite the same in character. The habit of the crystals obtained with fast-red E was platy on {001}, and the crystals were much twinned, though rarely to produce complete hexagons, the usual tendency being to produce somewhat elongated crystals joining up at the twinning plane at an angle of 60° with other similar units. The crystals were striated parallel with the lengths of the units, and the dye inclusions in the crystals were markedly dichroic, as predicted in Table 1 for the effect of dye adsorption on {100} of potassium nitrate.

Potassium nitrate has the small optic axial angle of 6°, but in spite of this it was possible to locate the optic axial plane (100) as perpendicular to the elongation and striations of the modified crystals. This indicated that the elongation and striation of the crystals were parallel with their *a* axis, and that twinning was on {110}. The colour of the dye inclusion was at a maximum when the electric vector was parallel to the optic axial plane, so that, if it is assumed that the dye molecules are located in a plane perpendicular to the modified plane, containing the flat nitrate ions, then the dye molecules must be adsorbed on {100}. In agreement with these deductions, it was possible to demonstrate the fitting of fast-red E on to {100}: both sulphonate groups fell into nitrate ion sites, and the hydroxy-group fitted within the radius of an ammonium ion (Fig. 1).

Amaranth in very high concentrations brought about the crystallisation of potassium nitrate as aggregates of small {001} hexagonal platy crystals, apparently pseudohexagonal triplets, not single crystals. Although often strongly coloured, the crystals did not show pleochroism save in a few isolated examples when small patches of colour showed dichroism probably indicating that the amaranth was adsorbed on {010}.

Amaranth does not fit on to {100} with all three sulphonate groups; a better fit is observed on {010} in which all sulphonate groups may be located in anionic sites (Fig. 2).

Sodium 1 : 4-*Diamino- and* 1 : 4 : 5 : 8-*Tetra-amino-anthraquinone*-2-*sulphonate.*—The diamino-compound produced exactly the same habit modification and pleochroism as fast-red E and by similar arguments it was shown to be adsorbed on {100}. The tetra-amino-derivative gave an even more platy habit; the {001} crystals were, however, coloured steel-blue and showed no striations or pleochroism to aid identification.

The diamino-compound fits well into {100}, the two amino-groups and the sulphonate group falling accurately into ionic sites. The tetra-amino-compound, however, will fit neither {100} nor {010}, but it fits excellently (032) with its four amino-groups replacing potassium ions. This plane is repeated owing to the pseudohexagonal symmetry about the *c* axis, which is an adequate explanation of the absence of pleochroism in the modified crystals.

Acid Alizarin-blue (C.I. 1063).—This dye in saturated solution in cold potassium nitrate solution influenced the crystallisation of the salt so that thin extended {100} plates with a matt surface to the naked eye, and with pleochroic dye inclusions, were produced. When microscopically examined under low power between crossed Nicols, the matt surface was found to be due to repeated twinning in the crystals. Parallel striations crossed each separate portion of the composite crystal, parallel to the {100} optic axial plane. The electric vector perpendicular to these striæ produced the maximum colour, so that the inference was that the dye molecules must be adsorbed on {010}. The sulphonate groups can be very accurately located on nitrate ionic sites in {010}.

Acid Magenta and Related Dyes.—Potassium nitrate underwent fairly strong modification of crystal habit on {001} with trisulphonated pararosaniline, but acid-magenta ND, similar, save for the addition of three *meta*-methyl groups to the molecule, had to be used in saturated solution to produce much effect. Trisulphonated Döbner's violet did not appear capable of modifying potassium nitrate in very significant degree. The *mm'*-disulphonated Döbner's violet, however, showed a habit-modifying power similar in strength to that of trisulphonated pararosaniline.

Definite conclusions were not drawn as to the likely mode of adsorption of these dyes, which gave strongly coloured non-pleochroic crystals.

On balance it appears that the {001} basal plane is most suited to the adsorption of acid-magenta. This is consistent with the absence of pleochroism in the modified crystals since the dye molecules adsorbed on {001} would show trigonal symmetry.

Trypan-red (Benzidine-3-sulphonate ⟶ 2 moles of amino-R-salt).—A very striking agreement observed when the 5-sulphonate groups of the trypan-red molecule were placed on the nitrate ions of {010} drawn to scale led to a prediction of strong modifying power for this dye. This was confirmed by the strong modification of habit to weakly coloured, apparently non-pleochroic {001} leaflets brought about by addition of trypan-red to a slowly crystallising solution of potassium nitrate.

It is possibly noteworthy that a quite good agreement with the pattern of nitrate ions in {100} is also shown by trypan-red, which may explain the lack of pleochroism, if any could be expected in the weakly coloured crystals.

It has not been possible to examine in detail some of the more interesting habit modifications of potassium nitrate owing to ignorance of the probable structures of the dyes concerned, *e.g.*, induline 2B.

Diagrammatical Illustrations of Adsorbed Dyes on Crystal Planes.—Diagrams of the two pinacoids {010} and {100} are reproduced (Figs. 1 and 2) and the dyes amaranth and fast-red E respectively are shown superimposed on the planes. In order to facilitate comparisons of dye structure drawn in accord with the available information with these planes, the ions are all numbered, and the ionic positions on which the polar groups of other dyes considered may be superimposed are given in Table 2. The sulphonate groups of the dyes are depicted merely as carbon–sulphur bonds, it will be understood that the planes of the oxygen triangles of the sulphonate groups are perpendicular to the plane of the dye molecules.

With respect to this and the following paper the author acknowledges the aid of Imperial Chemical Industries Limited, Dyestuffs Division, and Dr. E. K. Pierpoint, who prepared many dyes not listed in the Colour Index, and Professor W. Bradley, Dr. C. H. Giles, and Professor Wilson Baker, who gave many samples of obsolete commercial dyestuffs for testing.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
RESEARCH DEPARTMENT, NOBEL DIVISION,
STEVENSTON, AYRSHIRE.

[*Received, February* 13*th*, 1957.]