

945. *Crystal Symmetry, and the Adsorption of Dyes by Growing Crystals. Part I. Ammonium Nitrate IV.*

By JOHN WHETSTONE.

The suitability for dye adsorption of the principal low-index planes of ammonium nitrate IV is discussed in the light of the scheme proposed previously¹ to explain modifications of crystal habit by dyes. The evidence of dye adsorption on certain planes obtained by study of dye inclusions in modified crystals is consistent with the expectations from the above study of the crystal structure.

AMMONIUM NITRATE IV, when crystallised from saturated solutions containing a dissolved dye, frequently gives platy habit-modified crystals with pleochroic coloured regions containing adsorbed dye. Observations from some such crystals have already been used¹ in connection with the derivation of a theory of the mechanisms of crystal-habit modifications. This paper shows how the observed pleochroic inclusions with a variety of dyes of different structures are essentially related to the crystal symmetry of ammonium nitrate IV and the habit modifications produced.

Structure of Ammonium Nitrate IV Crystals.—Ammonium nitrate IV, stable between 32.3° and -18°, usually separates on very careful crystallisation as acicular pseudomonoclinic {110} needles or prisms, with bipyramidal terminations. Concordant X-ray crystallographic determinations of its orthorhombic structure have been described.^{2,3}

Planes on which planar dye molecules might preferentially be adsorbed are {100}, {010}, {001}, {101}, and {110}. Dye adsorption on one of the three pinacoidal forms {100}, {010}, and {001} would explain the frequent production of pleochroic dye adsorbates in modified ammonium nitrate IV crystals. The {001} plane consists of layers of ions all of one kind, but alternately regularly displaced by about 0.3 Å perpendicular to {001}. The {010} plane is of high reticular density and contains both ammonium and nitrate ions, all the latter being coplanar. The {100} plane is similar in type, but the nitrate ions are all perpendicular to {100}.

The {110} plane is composed of both anions and cations accurately centred, with the nitrate ions all inclined at about 45° to the plane. The reticular density is high, as also it is in {101} which, too, is composed of alternate anions and cations. These domal and prismatic forms, however, are obviously not suited to the production of pleochroic dye adsorbates.

According to ideas already expressed¹ it may be concluded that {010} is likely to be the pinacoid least suitable for adsorption of planar dye molecules, because the included nitrate ions and the planes of the oxygen triangles of the sulphonate groups of the dye would be mutually orthogonal. It is significant therefore that the most frequent habit modifications observed are on this plane, and {101}, {001}, and {100} are the forms most likely to be concerned in adsorption of dyes.

Adsorption on {110} should also be possible. This is a prismatic form, however, and it is probable that dye adsorption on {110} would merely accentuate the ordinary acicular habit of ammonium nitrate IV, which is not a very distinctive change.

The Possible Dual Nature of Habit Modifications.—A point not previously considered is the opportunity for the simultaneous restriction of growth rates on planes of two forms given by adsorption on planes of a third form. For example, when dye adsorption is on {100} retardation of growth should follow on {010} and {001}, to both of which (100) is an edge plane, and the final habit of the crystal would be an expression of the effect of the dye adsorption on the rates of growth in the *a*, *b*, and *c* directions. Owing to the close similarity of the polar-group spacing of the dye molecule and the ionic pattern of the crystal plane, overgrowth of adsorbed dye molecules on {100} is likely to be relatively easy; thus the rate of growth is likely to be less affected in the *a* than in the *c* direction. However, the

¹ Whetstone, *Trans. Faraday Soc.*, 1955, **51**, 973, 1142.

² Hendricks, Posnjak, and Kracek, *J. Amer. Chem. Soc.*, 1932, **54**, 2766.

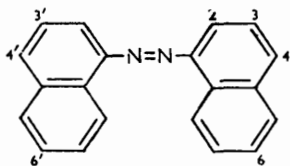
³ West, *ibid.*, p. 2256.

habit of the crystals is also influenced by their inherent growth tendencies in these directions. The final habit of the modified crystals is usually found to be more elongated in the a than in the c direction.

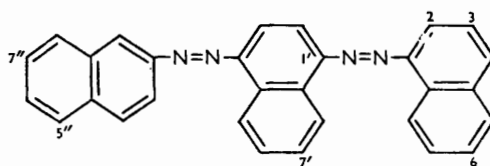
EXPERIMENTAL

Ammonium nitrate was crystallised slowly from slightly supersaturated solution at room temperature or at a constant temperature of 24° .

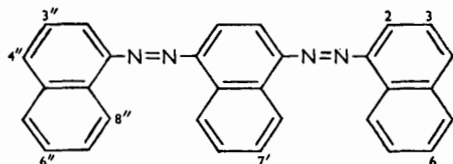
The habit modification on $\{010\}$ is usually very distinctive, because the modified crystals,



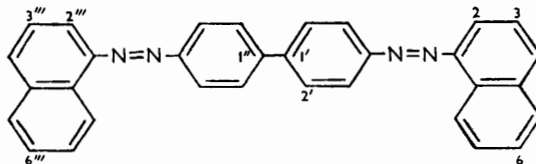
(I) a : 2-OH; 3:6:4'-(SO₃Na)₃
 b : 2-NH₂; 3:6:4'-(SO₃Na)₃
 c : 2-OH; 3:6:3':6'-(SO₃Na)₄



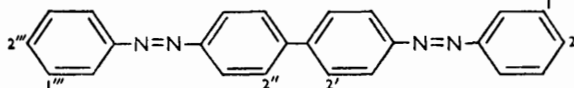
(II): 2-OH; 3:6:7':5'':7''-(SO₃Na)₅



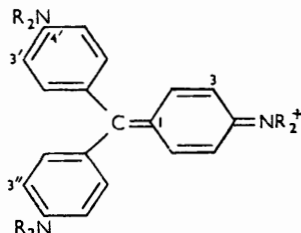
(III) a : 2-OH; 3:6:7':4'':6'':8''-(SO₃Na)₆
 b : 2-OH; 3:6:7':3'':6'':8''-(SO₃Na)₆



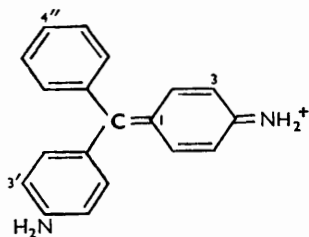
(IV): 2:2'''-(NH₂)₂; 3:6:2':3''':6'''-(SO₃Na)₅



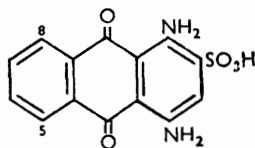
(V): 2:2'''-(OH)₂; 1:1'''-(CO₂Na)₂; 2':2''-(SO₃Na)₂



(VI) a : R = H; 3:3':3''-(SO₃Na)₃
 b : R = H; 4:(or 4' or 4'')-Me; 3:3':3''-(SO₃Na)₃
 c : R = H; 4:4':4''-Me₃; 3:3':3''-(SO₃Na)₃
 d : R = Me; 3:3':3''-(SO₃Na)₃



(VII) a : 3:3':4''-(SO₃Na)₃
 b : 3:3'-(SO₃Na)₂



(VIII)

lying on a microscope slide, show centred "acute bisectrix" interference figures when viewed conoscopically. For this reason systematic investigation of the relation between the structures of habit-modifying dyes and the crystal planes involved in the dye adsorption has been confined to the $\{010\}$ habit modifications of ammonium nitrate,

The key to the structures of the dyes is given in the Table.*

Acid Magenta and Related Dyes.—Acid magenta (Imperial Chemical Industries Limited) in concentration 0.2—0.5% by weight in a saturated ammonium nitrate solution below 32° was found readily to induce crystallisation of the salt as soft slimy lamellar aggregates. Other commercial samples of this dye behaved likewise, and also the commercial dye red-violet 5RS (*N*-monoethyl-acid magenta). On reduction and the concentration of dye to 0.01—0.005%, careful crystallisation usually yielded {010} platy or lath-like crystals elongated on {100} with a central rib or "hour glass" of pleochroic dye inclusion along the axis of elongation. Specially prepared dyes which gave similar effects were trisulphon-

Ammonium nitrate IV {010} Modification. Crystal habit-modifying dyes.

Structure *	Dye	Plane of adsorption (pleochroism) (fitting)	Location of polar groups on diagram of plane (X = SO ₃ ⁻ group)
<i>Azo-dyes</i>			
Ia	"Amaranth" or BA	{100} {100}	X(4')-10 OH(2)-7, X(3)-8, X(6)-3
Ib	D1F	{100} {100}	X(4')-10 NH ₂ (2)-7, X(3)-8, X(6)-3
Ic	α -Naphthylamine-3 : 6-disulphonate \rightarrow β -naphthol-3 : 6-disulphonate	{001} {100}	
II	EJ	{001} {001}	X(5'')-9, X(7'')-13, X(7')-15 X(3)-, X(6)-8
IIIa	E2D	{001} {001}	X(4'')-1, X(6'')-5, X(8'')-6 X(7'')-non-coplanar
IIIb	E2E	{001} {001}	X(3)-8, X(6)-12a (near) † X(3'')-12, X(6'')-15, X(8'')-11 X(7'')-non-coplanar
IV	"Trypan-red" (C.I. 438)	{100} {100}	X(3'')-5, X(6'')-2, X(2')-, X(3)-17, X(6)-21, NH ₂ -13
V	"Chromazol-yellow CRS" (C.I. 441)	{100} {100}	X(2')-7, X(2'')-11, CO ₂ H(1)-5 CO ₂ H(1''')-13
<i>Triphenylmethane dyes</i>			
VIa	Trisulphonated pararosaniline (C.I. 676)	{100} {100}	NH ₂ (4)-11, NH ₂ (4')-2, NH ₂ (4'')-8 X(3)-10, X(3')-6, X(3'')-8
VIb	Trisulphonated rosaniline ("acid magenta") (C.I. 692)	{100} {100}	ditto
VIc	Trisulphonated "new magenta" ("acid magenta ND") (C.I. 678)	{100} {100}	ditto
VI d	Trisulphonated methyl-violet (C.I. 680)	{100} {100}	NMe ₂ (4)-11, NMe ₂ (4')-2, NHMe ₂ (4'')-8 X(3)-10, X(3')-6, X(3'')-12
VIIa	Trisulphonated "Döbner's violet"	{100} {100}	NH ₂ (4)-1, NH ₂ (4')-10 X(3)-5, X(3')-9, X(4')-
VIIb	Disulphonated "Döbner's violet"	{100} {100}	NH ₂ (4)-5, NH ₂ (4')-7 X(3)-6, X(3')-7
<i>Anthraquinone dye</i>			
VIII	1 : 4-Diaminoanthraquinone-2-sulphonate	{100} {100}	NH ₂ (1)-7, NH ₂ (4)-6 X(2)-11

* The structures give the dyes as sodium sulphonates. As there is no generally accepted convention for numbering the ring systems of bisazo(or tetrazo)-compounds, the extreme right-hand systems in the formulæ shown have unprimed numerals, and primes, seconds, etc., are added as necessary as one reads towards the left. Ring systems having fixed numbering (*e.g.* benzidine, salicylic acid) retain that numbering primed as required.

† 12a is next anion in line with 12 in Fig. 2.

ated derivatives of the following: (a) new magenta (C.I. 678), (b) rosaniline (C.I. 677), (c) pararosaniline (C.I. 676) (only after modification of the pH to 3—4), and (d) methyl-violet (C.I. 680) (with difficulty). The leuco-bases of these dyes were not habit-modifiers, presumably because of their non-planar configurations. Attempts to prepare mono- and di-alkylated acid magenta in a pure state were unsuccessful. Trisulphonated rosolic acid only gave very weak modifications of ammonium nitrate IV. These dyes are all characterised by *meta*-sulphonation and *p*-amino-, *p*-alkylamino-, or *p*-hydroxy-groups on each phenyl group of the triphenylmethyl radical.

* Figures in parentheses after names of dyes, *e.g.*, (C.I. 692), give the reference in the Colour Index (F.M. Rowe, Society of Dyers and Colourists, 1924).

FIG. 1. (100) Plane, with superimposed structure (to same scale) of trisulphonated pararosanine.
(Plain circles are ammonium ions, double circles represent edgeways view of nitrate ions.)

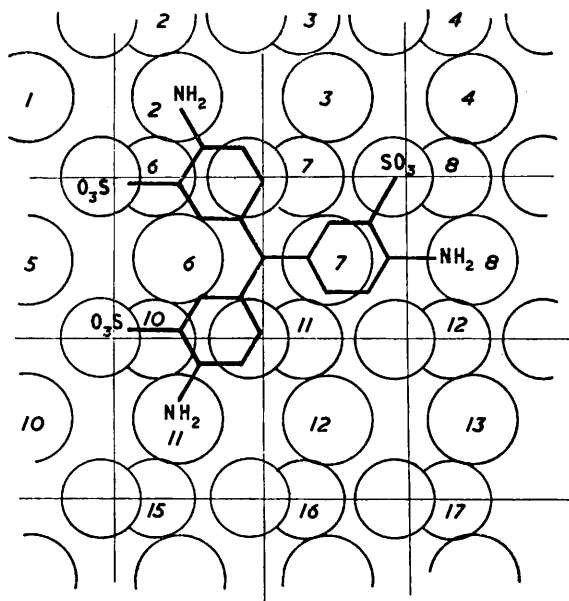
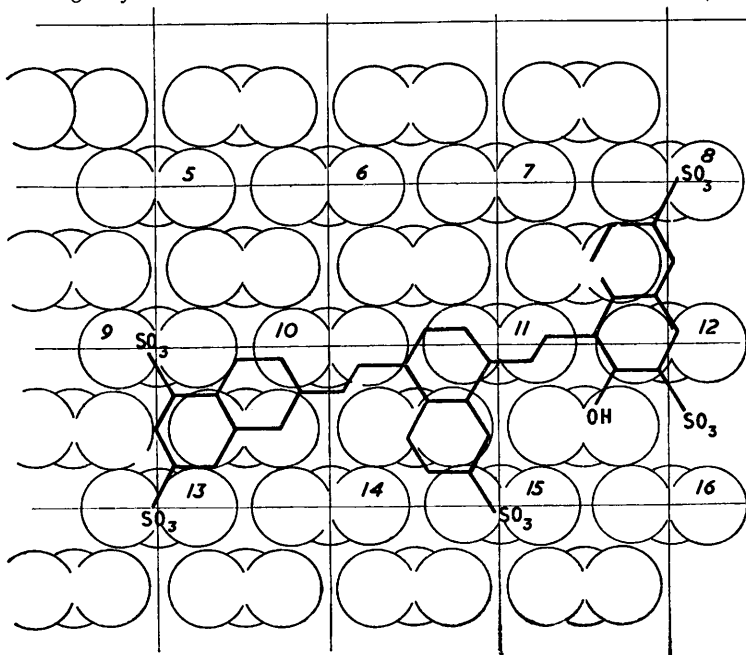


FIG. 2. (001) Plane, with superimposed structure (to same scale) of dye EJ. (Nitrate ions are shown edgeways. Unnumbered ions are 0.298 Å above those numbered.)



The optic axial plane {001}, deduced from the orientation of the melatopes of the interference figure, was in all cases parallel to the direction of elongation of the modified crystals, which must therefore be the *a* axis. Examination in polarised light showed that the colour was at a minimum when the electric vector was aligned with the optic axial plane, but it reappeared strongly when the optic axial plane was perpendicular to the electric vector.

Polarisation should be at a maximum when the electric vector is in the plane of the dye molecules, which must therefore be adsorbed on {100} or a plane almost parallel with (100).

Comparison of the acid magenta structure with possible planes for adsorption indicated that excellent agreement of the amino-groups with cation sites could be obtained on {130}; but since sulphonated diamino-triphenylmethane dyes such as trisulphonated Döbner's violet and *mm'*-disulphonated Döbner's violet gave precisely similar modifications to acid magenta, and these dyes could not be considered to be fixed in the lattice merely with two amino-groups replacing ammonium ions, it was most probable that adsorption was actually on {100}. It was possible to accommodate both anionic and cationic groups in ionic sites in this plane, and probably the notably high proportion of polar groups replacing ions in the crystal plane is responsible for the very strong habit-modifying tendencies of this type of dye.

The absence of polar groups on the third phenyl ring improves the fitting of *mm'*-disulphonated Döbner's violet as compared with acid magenta, which is consistent with the powerful habit-modifying effects observed with both the dye and its leuco-base. The reduced effect noted with trisulphonated Döbner's violet is probably connected with the *para*-sulphonation of the third phenyl ring, which results in a misfit between the dye structure and the (100) plane.

Pentasulphonated Aniline-blue.—The commercial sulphonated aniline-blues (C.I. No. 706) are mainly trisulphonates, and had but a slight modifying effect on ammonium nitrate IV. When these products were further sulphonated, in common with ink-blue A.S. prepared by direct sulphonation of aniline-blue, they showed more activity. A laboratory product, appearing from analysis to be slightly more than pentasulphonated, gave modified crystals of ammonium nitrate IV in the shape of thin {010} laths elongated on {100} and containing a central strip of pleochroic dye inclusion. The colour was at a maximum when the electric vector was aligned with the *a* axis. This is indicative of dye adsorption on {001}, which is in harmony with the highly sulphonated character of the dye, since the layers of ions in this plane are all of the one kind.

Amaranth or Naphthol-red S and Related Dyes.—Amaranth, or the pure dye preparation BA, induced the crystallisation of ammonium nitrate IV in soft, red, apparently lamellar masses but on closer examination the individual platy crystals appeared to be parallel aggregates of thin fibre-like crystals. With other isomeric dyes in which the same sulphonate group orientation as in amaranth is retained, *e.g.*, D1F, a similar structure was observed in the crystals of ammonium nitrate IV obtained, although owing to the lessened activity of some of these dyes the constituent fibres of the crystals were coarser. These fibres were oriented in the platy aggregate so as to present their {010} faces in all cases. Cinephotomicrographic observation of their growth process showed that they were formed by an initial parallel growth of fibre-like crystals close side by side followed by a filling in of the intervening spaces.

Microscopic examination of the amaranth-modified crystals showed that the direction of elongation of the constituent fibres was along the *a* axis, and that the fibrous crystals were markedly pleochroic. The colour was at a maximum when the electric vector was parallel with the *c* axis. This implies that the amaranth molecules are located on {100}, if the previous assumption that the dye molecules should be in a plane perpendicular to the habit-modified plane containing the coplanar nitrate ions is accepted.

It is fortunate that this particular instance permits testing of this hypothesis. The amaranth molecule can be fitted on {100} with its sulphonate groups occupying the sites of three nitrate ions. However, the dye can also be fitted flat on to {010}, although the oxygen triangles of the sulphonate groups are then perpendicular to the nitrate ions. The dye molecule when fitted on to {010} lies along the {101} direction. If this in fact represented the true mode of adsorption of amaranth on ammonium nitrate IV, then the maximum colour on rotating the modified crystals in polarised light should be developed when the electric vector is intersecting the fibres at an angle of about 50°, and not as was observed.

The Bis-azo-dye EJ (β -Naphthylamine-5 : 7-disulphonate \rightarrow α -Naphthylamine-7-sulphonate \rightarrow β -Naphthol-3 : 6-disulphonate).—The usual crystals of ammonium nitrate IV modified with EJ were quite dissimilar from those modified with amaranth. In place of the parallel growth of fibres, the initial growth of the crystals at fairly high rates appeared as dendrites branching at an acute angle (*ca.* 17°) and the space between the dendrites was then filled in with a platy growth. If the rate of growth of the crystals was slow, the dendritic growth was much less apparent or occasionally not observed, and a crop of thin, soft, lath-like crystals was obtained. A number of these crystals examined possessed a strongly coloured central rib, which was strongly pleochroic. The elongation of the laths was on {100}, and the colour of the crystals was found to be a maximum when the electric vector was parallel with their elongation, from

which the dye molecules must be located on {001}. The dye molecules may be fitted on to ions all at one level in {001}, the only non-fit being the 3-sulphonate group of the R-salt component. A dye E2F (β -naphthylamine-5 : 7-disulphonate \rightarrow α -naphthylamine-7-sulphonate \rightarrow β -naphthol-6-sulphonate), prepared to test the effect of omitting this apparently non-useful sulphonate group, was unfortunately almost completely insoluble, but its crystal habit-modifying powers were still apparent, which is indicative of exceptional potency in the very low concentration obtained.

The Bis-azo-dyes E2D and E2E (respectively α -Naphthylamine-4 : 6 : 8- or -3 : 6 : 8-trisulphonate \rightarrow α -Naphthylamine-7-sulphonate \rightarrow β -Naphthol-3 : 6-disulphonate).—These dyes gave similar crystals to those modified with E.J. Their characteristics and pleochroism were precisely the same, and the dye molecules could be located on {001} with all sulphonate groups but the central 7-sulphonate of E2E and the central 7-sulphonate and the 6-sulphonate of the R-salt component of E2D, occupying anion sites.

These dyes are examples of those in which the coplanarity of the component naphthalene ring systems is sterically hindered by the 8-sulphonation of the first coupling component. The strain in the molecules may be relieved if the central coupling component is forced out of coplanarity by the 8-sulphonate group; this, however, will still allow coplanarity of the first and the third naphthalene ring system to be maintained. Since the 7-sulphonate of the central α -naphthylamine component apparently does not assist in the dye adsorption when all the rings are forced into coplanarity, this would not appear to be a factor capable of materially altering the adsorptive forces between the crystal lattice and the other polar groups of the dye molecules.

The Aminoanthraquinonesulphonic Acids.—1 : 4 : 5 : 8-Tetra-aminoanthraquinone can be fitted accurately on to the modified plane {010} of ammonium nitrate IV, but this insoluble compound could not be expected to exert any effect on crystal habit. When sulphonated it became only slightly soluble, and modified ammonium nitrate IV crystals to laths on very slow crystallisation above pH 8, but this modification may also be explained by dye adsorption on {100}.

Sodium 1 : 4-diaminoanthraquinone-2-sulphonate was quite soluble and had a marked habit-modifying power for ammonium nitrate IV, platy {010} crystals often being obtained. On careful crystallisation, thin elongated plates with a central rib of pleochroic dye inclusion could be obtained, or sometimes with "hour-glass" inclusions. On examination in polarised light, it was found that the maximum colour was produced when the electric vector was perpendicular to the *a* axis. This indicates that the dye molecules must lie on {100}, and indeed it is possible to locate the two amino-groups on cation sites and the sulphonate group on an anion of {100}.

Chromazol-yellow C.R.S. (C.I. 441).—This dye, although only slightly soluble, was nevertheless capable of bringing about platy development of ammonium nitrate IV under favourable conditions of crystallisation. These thin {010} crystals obtained in the presence of the dye appeared almost completely colourless; but it was possible by less careful control of temperature on some occasions to obtain lath-like crystals of ammonium nitrate, with a central rib of adsorbed dye which was sufficiently conspicuous to allow observation of its colour changes in polarised light as the crystal was rotated. The pleochroism was identical with that of the previous example, so that dye adsorption must be on {100}; and, in fact, it is possible to fit the dye molecule in {100}, with its two carboxyl groups and its two sulphonate groups quite accurately replacing nitrate ions (disregarding any departure from coplanarity of the benzidine portion) and one hydroxy-group occupying an ammonium ion's site.

Cinephotomicrographic Study of Growth of Modified Ammonium Nitrate Crystals.—Cinephotomicrographic study of the growth of crystals of ammonium nitrate modified with acid magenta (0.2% in the saturated salt solution) showed clearly that their soft, slimy nature was due to dendritic growth processes.⁴ The dendritic crystals grow strongly in two directions inclined to one another at an acute angle (about 17°). This is consistent with the suppression of the crystals' growth on {100} and {001}, the growth now being most rapid on {101} and {102} which are planes of reasonably high ionic reticular densities, the normals being inclined to one another at 18° (approx.). The extreme complexity and thinness of these dendritically grown crystals is clearly responsible for the effectiveness of surface-coating ammonium nitrate with this dye in preventing the caking of ammonium nitrate in bulk.⁵ The same conclusions apply to a number of other crystals habit-modifying dyes.

⁴ Whetstone, *Ind. Eng. Chem.*, 1952, **44**, 2663.

⁵ Whetstone, B.P. 625,077/1949.

Diagrammatic Illustrations of Adsorbed Dyes on Crystal Planes.—Diagrams of the two pinacoids {100} and {001} most commonly concerned in habit-modification phenomena are reproduced (Figs. 1 and 2), and the dyes acid magenta and E J respectively are shown superimposed on the planes. In order to facilitate comparisons of other dye structures with these planes the ions are all numbered, and the ionic positions on which the polar groups of the dyes considered may be superimposed are given in the Table. 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.

It may be seen from the Table that it is possible to account for many habit modifications in terms of dye adsorptions in conformity with the pleochroism exhibited by the modified crystals, and that there are no apparent exceptions.

The few crystals without pleochroism examined have usually contained only very faint dye inclusions, so that there has been no suspicion of their abnormality. The only modified crystals not falling into line with the {010} platy kind have been fibrous growths obtained with azofuchsine G and one or two other dyes—unfortunately this type of growth has only been observed with one dye of verifiable structure and no conclusions are justifiable from consideration of such an isolated instance.

Interpretations of the plane of adsorption from coloured dye inclusions in crystals have in general been straightforward. The "Trypan-red" dyes are exceptions in that pleochroism was relatively slight with respect to the depth of colour of dye inclusions. Simultaneous adsorption on two pinacoids perpendicular to {010} may account for this. Where only one or two sulphonate groups have been concerned in the habit-modification phenomena, the fitting of models of the dye structure on to the probably concerned crystal planes will often not give a unique solution of the problem of the mode of adsorption of the dye molecules, so that the evidence of dyes containing more polar groups is in general more valuable. Some habit modifiers have not been considered owing to our ignorance of their structures, *e.g.*, sulphonated phthalocyanine which is adsorbed on {001}.

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 dyes for testing.

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

[Received, December 30th, 1955.]
