

862. *Crystal Symmetry and the Adsorption of Dyes by Growing Crystals. Part III.* Sodium Nitrate and Ammonium Sulphate.*

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The modifications of crystal habit produced in sodium nitrate and ammonium sulphate by dyes are described. The lack of pleochroic dye inclusions observed in the modified crystals is explicable by their respective trigonal and pseudo-hexagonal symmetry, with dye adsorptions on planes perpendicular or steeply inclined to their modified basal planes.

THE characteristics of a number of modified crystals of sodium nitrate and ammonium sulphate have been examined in the light of previous conclusions as to the effect of dye adsorptions on crystal habit.¹ They are considered together, because pleochroism is not normally encountered in the modified crystals.

The crystal structure of sodium nitrate departs radically from those of ammonium nitrate IV and the ordinary-temperature modification of potassium nitrate. The pseudo-hexagonal character of orthorhombic potassium nitrate, and the arrangement of its ions in

* Part II, preceding paper.

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

several layers in the unit cell parallel with the basal plane {001}, are, to a large extent, reproduced in sodium nitrate. The symmetry, however, has become rhombohedral, and the habit of sodium nitrate crystals has changed from the acicular and prismatic forms commonly shown by ammonium and potassium nitrates, to compact rhombs.

Ammonium sulphate is a member of a group of isomorphous salts including chromates and sulphates, all belonging to the orthorhombic system (space group V_h^{16}). The crystal-habit modifications of potassium sulphate and potassium chromate were investigated by Buckley,² who, however, predicted that ammonium sulphate would not be a suitable subject for investigation of its habit changes, compared with the above two substances, on account of its higher solubility and consequently its greater "salting out" powers, and also because the {010} plane, which in potassium chromate and sulphate was the one he had found to be enhanced by dyes, was already the predominant plane in the unmodified ammonium sulphate crystal. However, in this present work ammonium sulphate often was found to undergo habit modification with dyes on {001} instead of {010}, although the latter is in fact a frequent crystal-habit change with all salts examined of this group.

Modifications of Crystal Habit of Sodium Nitrate.—Sodium nitrate on crystallising at room temperature was strongly habit-modified to {0001} hexagonal plates by a few dyes, notably trisulphonated pararosaniline or acid-magenta, the acid-greens (Colour Index Nos. 669 and 670), ink-blue (C.I. No. 706), sulphonated Döbner's violet, induline, sodium 1 : 4 : 5 : 8-tetra-aminoanthraquinone-2-sulphonate, and a few bisazo-dyes of the naphthol-black B and Biebrich patent-black BO types (C.I. Nos. 315 and 320, respectively). Other dyes gave crystals approaching to a platy habit, notably solochrome-yellow YS (C.I. 197) and alizarin-brown (C.I. 167). In some cases where the dye was insufficiently soluble in the cold to give habit modifications positive effects could be observed on crystallising hot solutions saturated with the dye.

Dye Adsorption, and the Structure of Sodium Nitrate Crystals.—Examination of a model of the structure of sodium nitrate, built according to the X-ray crystal structure deduced by Wyckoff³ and revised by Tahvonen,⁴ shows that the planes most steeply inclined to the usually modified face {0001} are {10 $\bar{1}$ 0} and {11 $\bar{2}$ 0} and {10 $\bar{1}$ 1}, {10 $\bar{1}$ 2}, and {1014} progressively less steeply inclined. Owing to the trigonal symmetry, detectable pleochroism cannot be expected in crystals modified by adsorption of dye on these forms, or on any other forms the planes of which are repeated threefold about the zone axis. In conformity with this, pleochroism in the {0001} sections of modified sodium nitrate crystals was never observed. There was therefore no possibility of directly deducing planes of dye adsorption as before.⁵ It is, however, possible to account for dye adsorption by examining the degrees of coincidence between the polar groups of dye molecules and the ionic sites of the above crystal planes drawn to scale. It was concluded that of the above planes {10 $\bar{1}$ 2} and {11 $\bar{2}$ 0} are apparently most suitable for dye adsorption. As an example, Fig. 1 is a scale drawing of the {10 $\bar{1}$ 2} plane, with the dye molecule "EJ" (α -naphthylamine-5 : 7-disulphonate \rightarrow β -naphthylamine-7-sulphonate \rightarrow β -naphthol-3 : 6-disulphonate) superimposed. The coincidences between nitrate ion sites and sulphonate groups are remarkably good; this was noticed before the habit-modifying power of the dye was tested. The dye was found to be insoluble in cold saturated sodium nitrate solution, but dissolved in hot saturated solution and brought about the expected strong modification to {0001} plates on cooling the solution.

Two examples of crystal-habit modification of sodium nitrate with triphenylmethane dyes are of interest in view of the inferences as to the structures of the dyes concerned which may be made: (a) with ink-blue (b) with acid-green.

Modification of sodium nitrate with (a) ink-blue (C.I. 706). Samples of ink-blue AS manufactured by direct sulphonation of aniline-blue (triphenylated pararosaniline) were

² Buckley, *Z. Krist.*, 1934, **A**, **88**, 381; *Mem. Proc. Manchester Lit. Phil. Soc.*, 1939, **83**, 31.

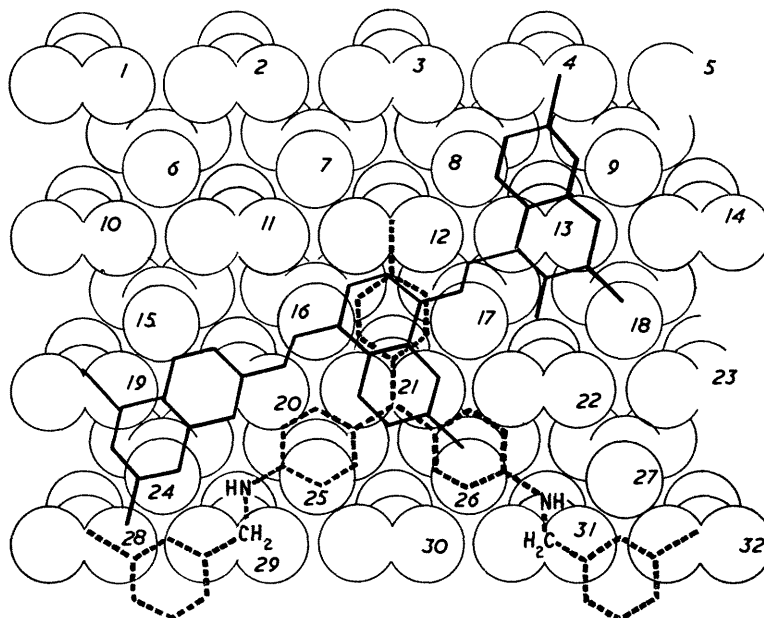
³ Wyckoff, *Phys. Rev.*, 1920, **16**, 149.

⁴ Tahvonen, *Ann. Acad. Sci. Fenn.*, Ser. A 1, *Math. Phys.*, 1947, **42**, 244.

strongly soluble in saturated sodium nitrate solution and brought about crystallisation of the salt as aggregates of {0001} platy crystals. Samples prepared by Sandmeyer's process⁶ were, however, almost completely insoluble in saturated sodium nitrate solution and did not affect the crystal habit. It was therefore suspected that the former sample had a higher degree of sulphonation than the latter, which was known to be trisulphonated.

Comparison of the dye structure with the ionic pattern of sodium nitrate {11 $\bar{2}$ 0} showed clearly that, in addition to an exact fitting of the *para*-sulphonate groups of the *N*-phenyl

FIG. 1. Dye EJ (solid outline) and acid-green GG (broken outline) on sodium nitrate {10 $\bar{1}$ 2}. Nitrate ions lie in a plane steeply inclined to the paper.



radicals on nitrate ion sites, *meta*-sulphonation of two phenyl groups in the rosaniline nucleus would exactly fit the nitrate ion pattern of the plane (Fig. 2). So would *ortho*-sulphonation of one of the *N*-phenyl groups. A pure sample of the Sandmeyer dye previously tested was further sulphonated for 1 hr. at 110° with 10% oleum, and a product apparently identical with ink-blue AS, in both its solubility and habit-modifying powers, was obtained. Analysis indicated about 5 sulphonate groups per molecule. It was evident that the dyes classified under C.I. No. 706 are likely to be of differing sulphonation, and consequently crystal-habit modifying activity, according to their method of preparation. Differences in degree of sulphonation are likely to be responsible in part at least for the large variations in activity of specimens of this dye from different sources observed by Buckley in his investigations with various salts.⁷

(b) *Acid-green M and GG extra* (C.I. Nos. 669 and 670). These two *N*-benzylated diaminotriphenylmethane derivatives were rather less active habit-modifiers than ink-blue, giving platy {0001} crystals on careful crystallisation from fairly concentrated dye solutions in saturated sodium nitrate solution (approx. 0.5% by wt. of dye).

The work of Fierz-David and others⁸ has indicated that *meta*-sulphonation expresses correctly the sulphonation of the benzyl groups instead of the *para*-sulphonation shown in the Colour Index formulæ of these dyes. In conformity with this view, it was found

⁵ Whetstone, *J.*, 1956, 4841; preceding paper.

⁶ Geigy and Co., B.P. 12,720/1892.

⁷ Buckley, *Proc. Manchester Lit. Phil. Soc.*, 1951, 92, No. 6, 1.

⁸ Fierz-David and Blangey, "Fundamental Processes of Dye Chemistry," Interscience Publ. Inc. New York, 1949, p. 305.

impossible, by using *para*-sulphonated models, to obtain satisfactory agreements with $\{11\bar{2}0\}$ or $\{10\bar{1}2\}$, but by using *meta*-sulphonated models the three sulphonate groups could easily be located accurately all at once on nitrate ions of the latter plane (Fig. 1).

Crystal-habit Modifications of Ammonium Sulphate.—With ammonium sulphate, as with potassium nitrate, differences in the appearances of $\{001\}$ modified crystals according to the dye responsible would be expected if any tendency to pseudo-hexagonal twinning is

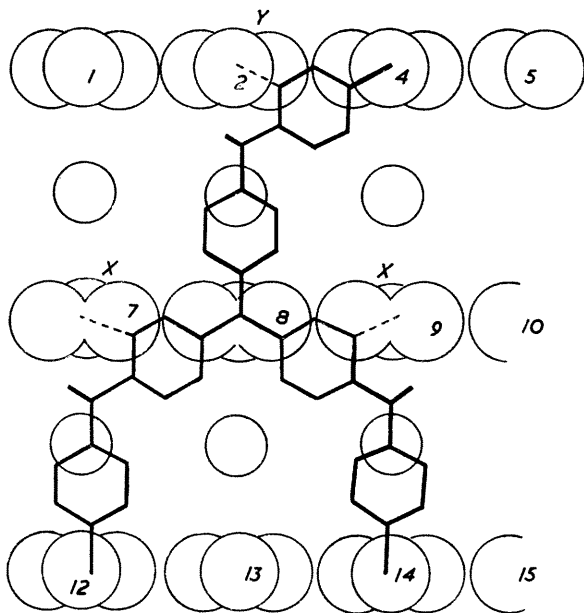
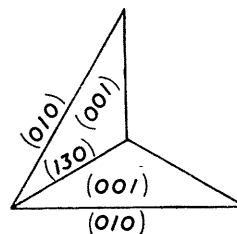


FIG. 2. Ink-blue AS on sodium nitrate $\{11\bar{2}0\}$. Single circles are sodium ions. Nitrate ions are in a plane perpendicular to the paper and are represented edge-wise, the oxygen atoms being shown. The broken lines at XX indicate ortho-sulphonation of the rosaniline nucleus. The broken line at Y indicates ortho-sulphonation of one N-phenyl group.

FIG. 3. Derivation of "arrowhead" twins with tartrazine.



present, but in fact no variation in the modified ammonium sulphate crystals comparable with those encountered with potassium nitrate was observed. No pleochroism should be obtainable from $\{001\}$ modified ammonium sulphate crystals owing to their pseudo-hexagonal structure, even in the absence of twinning, if simultaneous dye adsorptions on sets of planes related by the pseudosymmetry have occurred.

Examination of ammonium sulphate crystals grown in the presence of some dyes showed that habit modifications could readily be obtained to give $\{010\}$ platy rectangular crystals, or rectangular tablets. Other dyes gave very thin flexible hair-like needles, which apparently represent the ultimate habit-modification with very strong modifiers. These highly modified crystals are probably produced by the superimposition of the $\{001\}$ effect on the $\{010\}$ modification—it is not certain whether they are flattened on $\{001\}$ or $\{010\}$ since they were too thin for optical examination and too fragile to withstand manipulation. Crystallisation with low concentrations of these dyes invariably yielded $\{010\}$ plates, but the $\{001\}$ modification must have contributed considerably to the formation of the thin needles.

The pseudo-hexagonal symmetry of ammonium sulphate only once became evident in the formation of "arrowhead twins" from a saturated solution containing tartrazine on very long standing in a closed container; presumably the fine fibrous {001} modified crystals first deposited were unstable with respect to larger crystals, and dissolution of the former was followed by the very slow growth of the arrowhead twins. The plane of twinning was {130}, and the crystals were flattened on {001} (see Fig. 3).

It is noteworthy that azo-dyes containing a β -naphthol- or β -naphthylamine-3 : 6-disulphonate component usually appear to be especially effective as habit-modifiers for ammonium sulphate and give the {001} type of modification; quite a long list of these dyes can be compiled (see Table). It is thus probable that the inter-sulphonate distance in this

Some crystal-habit modifications of ammonium sulphate with dyes.

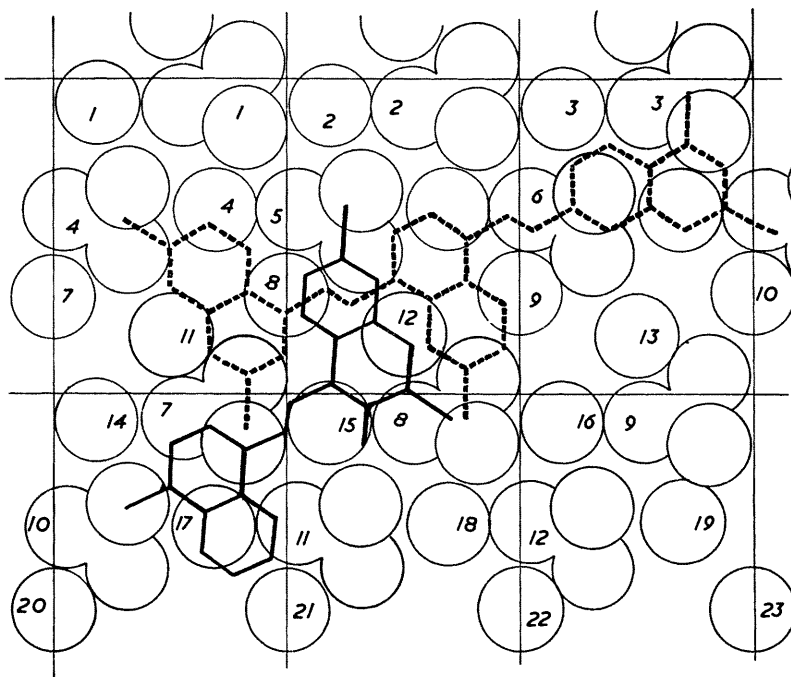
No.	Dye	Solubility *	Habit modification	Description of crystals
C.I. 184	Amaranth	Sol.	{001}	Fine, flat, soft needles
„ 188	Chromotrope 2B	Sol.	{001}	„ „
„ 197	Solochrome-yellow YS	Sol.	{001}	„ „
„ 315	Naphthol-black B	V.S.S.	{001}	Needles
„ 320	Biebrich Patent-black BO	Sol.	{001}	Fine, flat, soft needles
„ 438	Trypan-red	S.Sol.	{001}	„ „
„ 640	Tartrazine	Sol.	{001}	„ „
„ 692	Acid-magenta	Sol.	{010}	Rectangular plates
„ 706	Ink-blue AS	S.S.	{010}	Rectangular tablets, plates
BB	α -Naphthylamine-2-sulphonate \rightarrow β -naphthol-3 : 6-disulphonate	S.S.	{001}	Fine, flat, soft needles
BA	α -Naphthylamine-4-sulphonate \rightarrow β -naphthol-3 : 6-disulphonate	Sol.	{001}	„ „
BIF	α -Naphthylamine-3 : 6-disulphonate \rightarrow β -naphthol-3 : 6-disulphonate	S.S.	{001}	Acicular, flattish
DIF	α -Naphthylamine-3 : 6-disulphonate \rightarrow β -naphthol-4-sulphonate	Sol.	{001}	Fine, flat, soft needles
AIF	α -Naphthylamine-3 : 6-disulphonate \rightarrow β -naphthol-6-sulphonate	S.S.	{001}	Acicular, flattened
GA	α -Naphthylamine-4-sulphonate \rightarrow β -naphthylamine-3 : 6-disulphonate	Sol.	{001}	Fine, flat, soft needles
GB	α -Naphthylamine-3 : 6-disulphonate \rightarrow β -naphthylamine-3 : 6-disulphonate	S.S.	{001}	Fine, soft needles
GC	Sulphanilic acid \rightarrow β -naphthylamine-3 : 6-disulphonate	Sol.	{001}	Fine, flat, soft needles
HC	α -Naphthylamine-3 : 6-disulphonate \rightarrow α -naphthol-4-sulphonate	S.S.	{001}	Fine needles
HD	Sulphanilic acid \rightarrow H-acid	Sol.	{001}	Fine, flat, soft needles
HE	α -Naphthylamine-4-sulphonate \rightarrow H-acid	Sol.	{001}	„ „
EJ	β -Naphthylamine-5 : 7-disulphonate \rightarrow α -naphthylamine-7-sulphonate \rightarrow β -naphthol-3 : 6-disulphonate	Sol.	{001}	„ „
E2E	α -Naphthylamine-3 : 6 : 8-trisulphonate \rightarrow α -naphthylamine-7-sulphonate \rightarrow β -naphthol-3 : 6-disulphonate	Sol.	{001}	„ „
E2C	α -Naphthylamine-3 : 6 : 8-trisulphonate \rightarrow α -naphthylamine \rightarrow β -naphthol-3 : 6-disulphonate	Sol.	{001}	„ „

* S = soluble; S. sol. = slightly soluble; V.S.S. = very slightly soluble.

type of dye intermediate is reproduced accurately in some of the inter-sulphate ion distances in the ammonium sulphate structure. Fig. 4 illustrates the fitting of models of amaranth and the bisazo-dye "EJ" on to {100}. The structural determination of ammonium sulphate used was due to Ogg.⁹ More than this simple correspondence of the 3 : 6-sulphonate groups of naphthalene with ionic sites is necessary, however, to give habit

⁹ Ogg, *Phil. Mag.*, 1928, 5, 354.

FIG. 4. The bisazo-dye EJ (broken outline) and amaranth (solid outline) on ammonium sulphate {100}. Single circles are ammonium ions. Sulphate ions are shown in projection perpendicular to the paper.



modifications of any magnitude, because the dye intermediates themselves such as R-salt have but a negligible effect on the crystal habit of ammonium sulphate.

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