

*An X-Ray Examination of Iodo-Succinimide.*

By KATHLEEN YARDLEY, M.Sc.

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[PLATES 22 AND 23.]

Succinimide\* crystallises in the orthorhombic system with eight asymmetric molecules in the unit cell. When, however, the hydrogen of the -imide group is replaced by iodine, the resulting compound crystallises in the tetragonal system, its unit cell showing no resemblance whatever to that of the parent substance. Groth† describes the crystals of iodo-succinimide as—

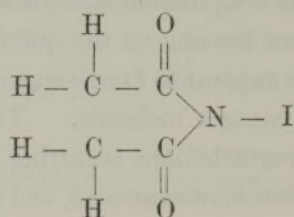
Ditetragonal pyramidal.

$$a : c = 1 : 0.8733.$$

Dr. Tutton‡ has remeasured the axial ratio with great precision and found

$$a : c = 1 : 0.8739.$$

Very fine small crystals were grown from acetone; the outward form of these showed clearly their polar character (fig. 1). A preliminary measurement of the density was made by the suspension method (the liquid used being a mixture of benzene and methylene iodide in variable proportions), and it was found to be 2.41 grs./c.c. A more accurate determination by Tutton§ gave 2.408 grs./c.c. The structural formula of the molecule is



and its molecular weight is therefore 225. The spacings of planes in three principal zones having indices  $\{hkO\}$ ,  $\{hOl\}$ ,  $\{hhl\}$  were measured on the Bragg ionisation spectrometer, using a Coolidge tube having a rhodium anticathode. Considerable discrepancies were found between the values actually determined

\* K. Yardley, 'Roy. Soc. Proc.,' A, vol. 105, p. 451.

† P. Groth, 'Chemische Krystallographie,' vol. 3, p. 271.

‡ A. E. H. Tutton, 'Roy. Soc. Proc.,' this volume, following paper.

§ *Loc. cit.*

and those calculated from the available crystallographic data. The spectrometer readings were verified by comparison with those calculated from a rotating crystal photograph and from a powder photograph, kindly taken by Mr. Bernal and Mr. Plummer respectively.

The unit cell deduced from X-ray measurements alone differs from that derived from external measurements alone in a way that can best be described by means of a diagram (fig. 2). The true crystallographic cell is shown by full, the cell defined by the original axial ratio is indicated by dotted, lines. It will be noted that both cells occupy the same volume, but the dotted cell

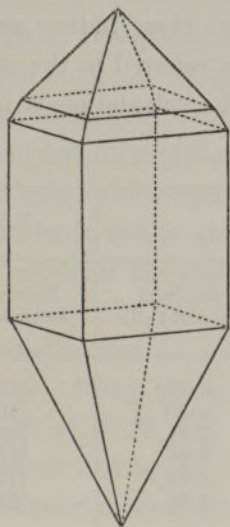


FIG. 1.

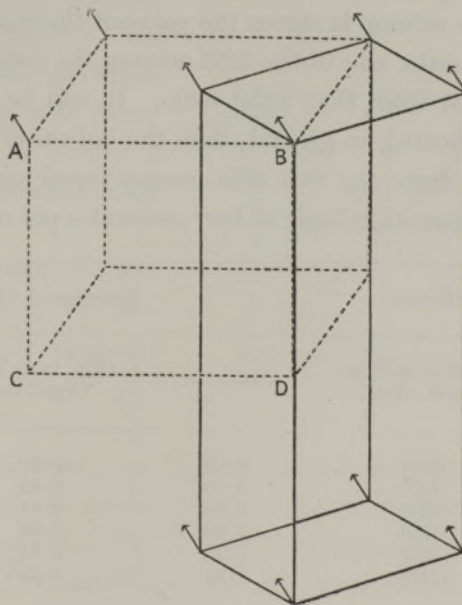


FIG. 2.

has the square faces centred, while its  $c$  axis is only one-half of the length of the true  $c$  axis. It is therefore incomplete, and if repeated through space parallel to itself would not build up the correct structure. The axial ratio recorded by Groth is the ratio  $AB : AC$ . The true axial ratio is simply related to it:—

$$\begin{aligned} a : c &= \frac{AB}{\sqrt{2}} : 2 AC \\ &= AB : 2\sqrt{2} \cdot AC \\ &= 1 : 2.469 \end{aligned}$$

$$[a : c = 1 : 2.471. \text{—Tutton}.]$$



The number of molecules per unit cell is then calculated from the usual formula :

$$a^2 \cdot c \cdot \rho = n \cdot M \cdot 1.65.$$

Using the observed value  $a = 6.29$  A.U., together with Tutton's values of the axial ratio and density, we find

$$n = 3.99 \text{ (4 mols./cell).}$$

This means that each of the arrows in fig. 2 represents a group of four molecules. In the following table comparison is made between the observed spacings and those calculated from the true crystallographic cell. In the fourth column is shown the value of the spacing calculated from the erroneous axial ratio, and in the fifth column the indices of the form referred to the cell derived from that axial ratio. It will be seen that these indices are more complicated, in general, than the indices of the form referred to the true unit cell. Since the two cells occupy equal volumes, the calculation is made in each case on a basis of four molecules per cell.

Form.	Spacings of Planes.			Form.
Referred to True Cryst. Cell.	Observed.	Calc. from True Cryst. Cell.	Calc. from Original Cell.	Referred to Original Cell.
{100}	6.29	6.29 <sub>5</sub>	6.29 <sub>5</sub>	{110}
{110}	4.40	4.45	8.90	{100}
{120}	2.80	2.81 <sub>5</sub>	2.81 <sub>5</sub>	{130}
{130}	1.98	1.99	3.98	{120}
{230}	1.73	1.74 <sub>5</sub>	1.74 <sub>5</sub>	{150}
{140}	1.51	1.53	1.53	{350}
{001}	3.83	15.55	7.77 <sub>5</sub>	{001}
{104}	3.31	3.31	3.31	{112}
{103}	4.00	4.00	2.00	{223}
{102}	4.90	4.89	4.89	{111}
{203}	2.70	2.69	1.34 <sub>5</sub>	{443}
{101}	5.83	5.83 <sub>5</sub>	2.92	{221}
{201}	3.06	3.08 <sub>5</sub>	1.54	{441}
{301}	2.05	2.07	1.03 <sub>5</sub>	{661}
{111}	4.24	4.28	4.28	{401}
{223}	2.04	2.04 <sub>5</sub>	1.02	{803}
{112}	3.85	3.86	3.86	{201}
{113}	3.37	3.38	1.69	{403}
{114}	2.94	2.93	5.86	{101}

It will be seen from the above table that all the spacings observed have the full calculated values (referring now to the true crystallographic cell only), except that of the (001), which appears to be quartered, since only fourth,

eighth and twelfth order reflections were found. If the crystals really possess ditetragonal pyramidal symmetry, this quartering of the (001) spacing can have no structural (*i.e.* geometrical) significance, and the crystals must belong to the space-group  $C_{4v}^1$ , being based on the Bravais lattice  $\Gamma_t$ .<sup>\*</sup> Any other space-group in this class would involve the disappearance of the odd orders of certain sets of planes, but these have all been actually found present. The space-group  $C_{4v}^1$  possesses four pure planes of symmetry intersecting in a fourfold rotation axis, eight asymmetric units being required to build up the symmetry of the unit cell (fig. 3). Since there are but four molecules in the unit cell of iodo-succinimide, each molecule would possess a plane of symmetry. The corresponding points of all four molecules would lie in one plane, the (001), and therefore each molecule would have to occupy a length of  $15.55 \text{ A.U.}$ , though possessing a cross-section of but  $(6.29/2)^2$  units.

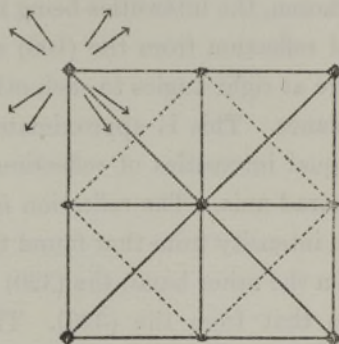


FIG. 3.

Considering the structural formula of iodo-succinimide, it seems quite impossible to give such a molecule the extraordinarily elongated shape required by the above conclusions, and at the same time to retain in it a plane of symmetry. Using the generally accepted values for the atomic diameters, the length of  $15.55 \text{ A.U.}$  could only be attained by placing all the atoms in the molecule end to end in a kind of long chain, and it is obvious that from a chemical point of view this is quite inconceivable. The only possible deduction is that the symmetry of the crystals is *not* ditetragonal pyramidal. The crystals, however, are certainly polar, and therefore the only other class to which they can belong is the pyramidal class (tetragonal tetartohedry).

The observed facts, namely, that there are four molecules per cell, and that the spacing of the (001) plane is apparently quartered, though every other plane shows a normal spacing, are additional evidence in favour of this class. A surer test, however, is the comparison of the intensities of reflection from pairs of planes, one on either side of the supposed plane of symmetry; for example, from the (210)  $(\bar{2}10)$ , &c. This was done on the Bragg spectrometer with the following result:—

<sup>\*</sup> W. T. Astbury and K. Yardley, "Tabulated Data for the Examination of the 230 Space-Groups by Homogeneous X-rays," 'Phil. Trans.,' A, vol. 224, p. 221.



Plane.	Approx. Intensity of Reflection.	Plane.	Approx. Intensity of Reflection.
(100)	12	(310)	6
(010)	12	( $\bar{3}$ 10)	7
(110)	22	(320)	11
( $\bar{1}$ 10)	20	( $\bar{3}$ 20)	5
(210)	3	(410)	3
( $\bar{2}$ 10)	18	( $\bar{4}$ 10)	3

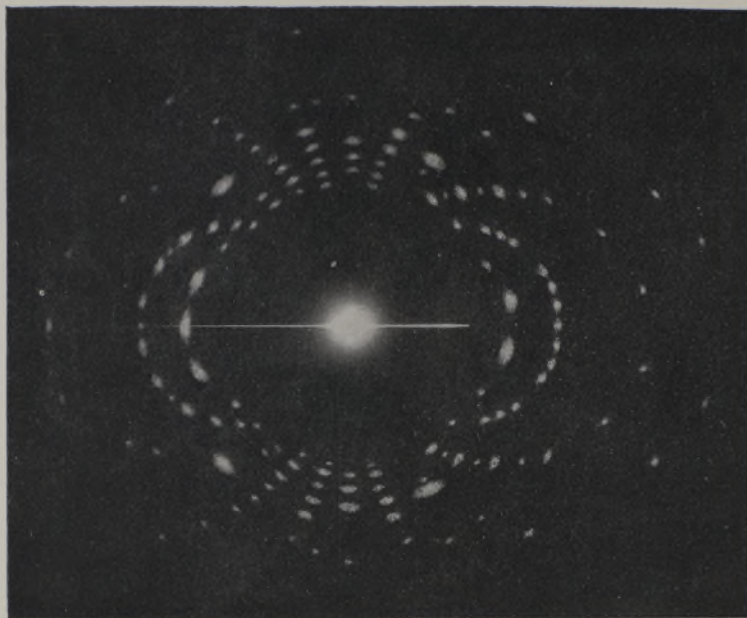
It will be understood, of course, that the first of these numbers is arbitrarily chosen, the intensities being then proportional to the numbers. The intensities of reflection from the (100) and (010) should be the same, since these planes are at right angles to each other; the same should hold for the (110) and ( $\bar{1}$ 10) planes. This is approximately the case. The (120) ( $\bar{2}$ 10), etc., also showed equal intensities of reflection, as would be expected from the existence of a tetrad axis. The reflection from the (210) plane was, however, quite different in intensity from that found for the ( $\bar{2}$ 10), being only about one-sixth as strong. On the other hand, the (320) plane gave a reflection more than twice as strong as that from the ( $\bar{3}$ 20). These results completely negative the possibility of the existence of planes of symmetry parallel to the {100} and {110}.

As a final confirmation a Laue photograph was kindly taken by M. Mathieu, the X-rays being perpendicular to the (010) face, and the *c* axis vertical. Since the X-rays always add a centre to the crystal symmetry, such a photograph would show a horizontal and a vertical plane of symmetry in the case of a crystal belonging to the class  $C_{4v}$ , but a horizontal plane only, if the crystal belongs to the class  $C_4$ .

The photograph (Plate 22), and its gnomonic projection (Plate 23), while showing clearly that the crystal used was untwinned and well set up, obviously possess only one plane, the horizontal plane of symmetry introduced by the addition of a centre.

Assuming that the quartering of the (001) spacing has a geometrical significance, the space-group to which iodo-succinimide belongs is either  $C_4^{2,*}$ , which possesses a tetrad screw axis of translation  $c/4$ , or  $C_4^4$ , which has an axis similar but in the opposite rotatory sense (fig. 4). In fact, both the right-handed and the left-handed forms should be possible, though as no vicinal faces have yet been observed it is not possible to distinguish between them from external form alone.

\* W. T. Astbury and K. Yardley, *loc. cit.*



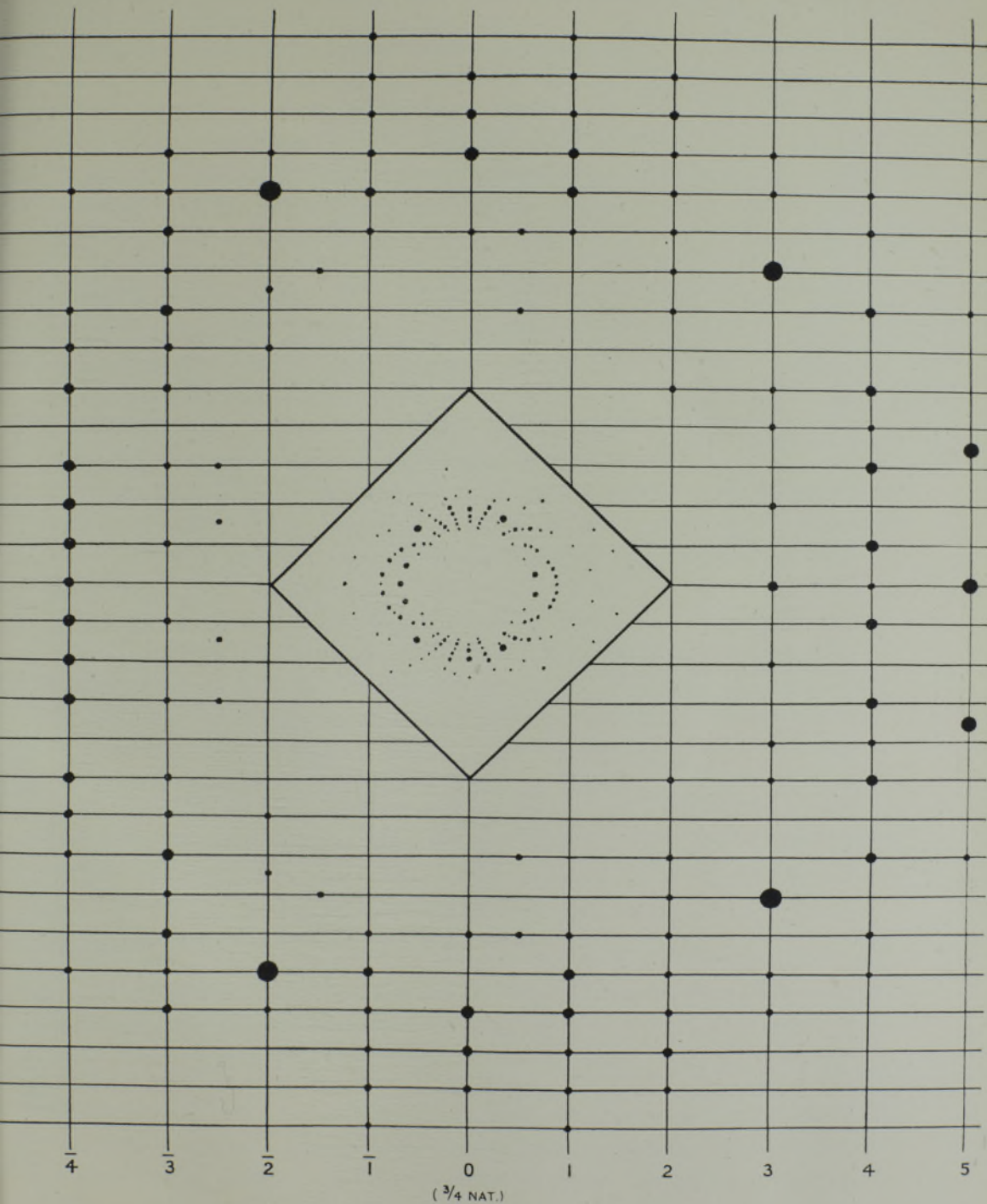
Laue photograph of iodo-succinimide.

PLATE 23, opposite, shows gnomonic projection of Laue photograph. Inset in centre is a copy of the actual photograph. The absence of any vertical plane of symmetry is quite obvious. On the projection, planes lying in one zone give spots lying along a straight line. The plane of projection is normal to the  $b$  axis.



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*Roy. Soc. Proc., A, vol. 108, Pl. 23.*



If the above conclusions are correct, the crystals belong to one of the eleven classes possessing only axes and no planes or centres of symmetry, and they should therefore show optical activity. As there were no available data concerning the optical properties, Dr. Tutton very kindly undertook this part of the investigation, and also carefully remeasured the axial ratio and density. His results, which are embodied in the following paper, fully confirm the X-ray measurements and clearly prove the class to be pyramidal, as distinct evidence of optical activity was found.

Twinning was observed on the basal plane and also, more frequently and completely, on the prism faces  $\{100\}$ . Groth records a cleavage parallel to the  $\{102\}$  planes and there was also an imperfect cleavage parallel to the prism faces. Consequently it was fairly easy to obtain thin slips parallel to one of these faces.

The crystal slip used by M. Mathieu was less than 0.5 mm. thick. It was not found possible, however, to obtain by grinding any truly parallel section perpendicular to the  $c$  axis thin enough for a Laue photograph to be taken in that direction, though many attempts were made. In the course of one such attempt the etch figures made by acetone on the basal plane were observed to be pyramidal pits with square bases, the sides of which were parallel to the prism faces. The etch figures on the prism faces are described by Groth as isosceles triangles, the vertices of which point towards the negative end of the  $c$  axis. Thus the evidence of etch figures is not to be trusted in the case of these crystals as an indication of crystal class; the etch figures, in fact, show *more* symmetry than the crystals actually possess.

In conclusion, I wish to thank Prof. Sir William Bragg for the kind interest he has taken in this work, and to acknowledge my indebtedness to the Scientific and Industrial Research Department and to the Royal Institution for the financial and laboratory facilities supplied by them. My thanks are also due to Dr. Tutton, of Cambridge, and to the various workers at the Davy-Faraday Laboratory, who have given me valuable advice and assistance. Messrs. Boots, manufacturing chemists, were kind enough to present me with the material used in this investigation.

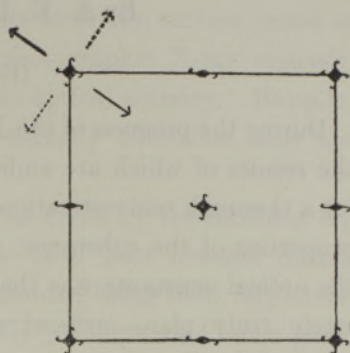


FIG. 4.