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*The construction and use of an X-ray goniometer.
Crystal-structure of glyoxaline compounds.*

(With Plate I.)

By GILBERT GREENWOOD, M.Sc.

Late John Harling Fellow in the University of Manchester.

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IN ordinary circumstances crystal-angles are measured by means of light reflected from the crystal-faces. In the partial or complete absence of faces the determination of axial ratios and angles may be impossible. In a recent investigation¹ of certain derivatives of glyoxaline, an example of this was found. It was, in fact, the substance glyoxaline itself, which always occurred as long prisms having four faces in the prism-zone; the ends of the prisms were jagged and rough, and no signs of optically reflecting-planes could be found on these ends. In such a case, X-ray methods of investigation are now available, and the problem in question is the determination of the dimensions of the unit-cell, not the complete X-ray investigation of the structure. Many substances, which do not exist in a suitable state for measurement by the crystallographer, have been investigated and the unit-cell

¹ G. Greenwood, *Min. Mag.*, 1925, vol. 20, p. 393.

determined, even if the exact atomic arrangement has not been found. Among such substances are to be found crystalline organic powders, metallic crystals, either in the form of conglomerate masses or wires, and also solidified gases like ethane. The photographic and ionization spectrometric methods, the powder photograph, and the rotating crystal method have all been used. In this paper the point of view is that of one who has generally worked with the ordinary goniometer rather than that of the X-ray analyst.

The object has been to build a somewhat composite goniometer in which the source of light is replaced by a source of X-rays, and the telescope by an ionization chamber, and to test such an instrument for ease and convenience of working. It was found when a zone was adjusted on the goniometer that the spacings of many faces in this zone could be rapidly determined, and thus the instrument also provides a good method of fixing the space-group of a crystalline substance, by a method of the spectrometric type. The new apparatus is shown in the photograph (Plate I). The graduated upper circle is fixed to a brass rod which carries at its lower end an adjusting goniometer-head of the usual type. Thus when the crystal is rotated, the graduated circle also moves and the reading is made against a fixed vernier. The lower graduated circle is just as in the older forms of X-ray spectrometer and the ionization chamber moves round this circle. In making the initial adjustments it is, of course, essential to bring the axes of rotation of the two scales into coincidence. This was achieved by setting pins exactly in the axes of rotation of both scales by means of a telescope. The upper scale was now moved about slightly until the tips of the pins when viewed in the telescope were exactly in the same vertical line. On the lower brass disc arrangements were made for the temporary mounting of two brackets carrying a telescope and a collimator. These were adjusted so that their optical axes meet in the axis of rotation of the two graduated circles and also lie in a plane perpendicular to it. In this way, in conjunction with the upper scale, they form a goniometer. Thus a small crystal can be mounted and adjusted on the instrument with all the rapidity of the ordinary goniometer. The slow-motion tangent-screws are in the form of a worm-thread working in a toothed groove which runs all round the graduated discs. In this way the same rotation of the screws always produces the same angular rotation of the circle. The tangent-screw of the upper circle bears a little pulley wheel which is driven by a large wheel above, which, in turn, is driven by a motor. By using suitably sized wheels and gearing arrangements it is possible to drive

the crystal round at the required rate. The field and armature of the motor are run on different circuits, thus by reversing the armature current it is possible to reverse the direction of rotation of the crystal. In this apparatus monochromatic Mo-radiation is used. It is generated by a Coolidge bulb, mounted on an adjustable holder, inside a large lead box. The bulb is run by means of a coil and a 'mercury-gas' break. The width and divergence of the X-ray beam is limited by means of two sets of slits, one close up against the lead box and the second as near to the crystal as possible.

In using the apparatus the crystal is mounted on wax on the holder and the zone-axis of the zone in question adjusted to be vertical by means of the telescope. It was found that an accurate adjustment can be made using the telescope alone without actually reflecting images of the collimator-slit. It is then very easy to find one of the large reflections from one of the more important faces in the zone, by sweeping the crystal in an appropriate position, and using the ionization chamber with its slits wide open. The exact crystal setting is then measured in the usual manner reflecting to the right-hand side. The chamber is then taken round to the same setting on the left-hand side, the reflection again found, and its position measured. In most cases quite small crystals—often only a few millimetres in size—are used. Under these circumstances, most of the reflection comes from the inner planes of the crystalline structure. This state of affairs is often further enhanced by the fact that the little crystals likely to be investigated are very transparent to X-rays. The result is that the effect of a badly cut surface mentioned by W. H. Bragg¹ does not come into play, and it is quite easy to recognize the two reflections as being the same. The mean of the two crystal settings gives the position of the normal to the crystal-face, with respect to the upper circle. A measurement of this sort may be made with any order of the reflections, e. g. the second order may be used if it is large or otherwise more convenient than the first. Another face is now examined in exactly the same way and the position of its face-normal measured on the upper graduated disc. The angle between these two settings is the ordinary interfacial angle of crystallography. A second type of angular measurement must now be made. This is the measurement of the glancing-angle. The procedure is essentially the same as in the X-ray spectrometers now in use. The chief point is to make sure that the true glancing-angle has been found, and that no intermediate spectra exist.

¹ W. H. Bragg, *Phil. Mag.*, 1914, ser. 6, vol. 27, p. 888.

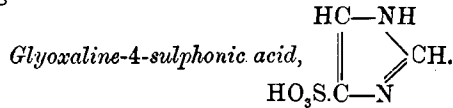
The first set of measurements when a sufficient number have been made serves to fix the axial ratios and axial angles. However, these axial ratios do not necessarily correspond to the true unit-cell, but may be this unit with one or more of its edges multiplied by a simple factor. The two sets of measurements taken in combination give means of finding this true unit. The easiest procedure is graphical—to make a drawing of the traces of the planes perpendicular to a plane containing two of the axes. In this way we can find the unit lengths along the axes which are consistent with the largest of the spacings measured for this zone. We may, and probably shall, find that a unit-cell of this size makes certain spacings multiples of that actually found. This is because the particular crystalline arrangement causes a halving, &c., of the true spacing. It is due to the presence of gliding-planes of symmetry, &c., in the structure, and this action has been well illustrated in a simple case by W. T. Astbury and K. Yardley.¹ Other zones and spacings must be considered in the same manner, and thus the three dimensions of the unit-cell can be definitely fixed and the spacial network is determined. The set of normal and divided spacings is dependent on the presence of glide-planes of symmetry, &c., and thus on the space-group. Very often a set of spacings is characteristic of a space-group, and thus the space-group of the particular structure can be found. Sometimes, however, a set of spacings is consistent with several space-groups.

In determining the space-group the tables given by P. Niggli² or W. T. Astbury and K. Yardley may be used. A direct method is also useful. The perpendicular distance from the origin to any plane ($g h k$) passing through the points whose numerical co-ordinates are x, y, z , is given by $p = gx + hy + kz$, p also being in the numerical system and a unit value corresponding to the normal spacing of a unit-cell. Using the book of R. W. G. Wyckoff, 'The analytical expression of the results of the theory of space-groups' (1922), in which the numerical co-ordinates of all the points occurring in the space-group are given, we can easily determine whether a particular spacing is subdivided or not. Knowing the system, and sometimes even the crystal-class, we can often, even with quite a small number of spacings, determine which of the space-groups is concerned. This depends on the fact that the method is one of elimination.

¹ W. T. Astbury and K. Yardley, *Phil. Trans. Roy. Soc. London, ser. A*, 1924, vol. 224, p. 221.

² P. Niggli, *Geometrische Kristallographie des Diskontinuums*. 1919, p. 498.

The two substances described below have been investigated with the help of the new goniometer.



This substance, for which the apparatus was first used, has already been described crystallographically.¹ It was there found that the crystals are tetragonal, though they usually exhibit only the forms {001} and {110}. However, other very small facets were found, and from a consideration of these faces the crystal-class was stated to be ditetragonal alternating. This statement has now been absolutely confirmed, and the crystalline structure proved to belong to the space-group with Schoenflies's notation V_d^4 , which is a ditetragonal alternating one.

The following table gives the result of the search for spectra. All spectra are referred to the primitive translations of the unit-cell.

(110) absent (100) absent (230) present (221) absent (402) present (001) absent
 (220) present (200) present (180) present (442) present (603) absent (002) present
 (330) present (300) absent (260) trace (663) absent (102) present (003) absent
 (440) present (400) present (390) absent (101) present (204) absent
 (550) present (140) present (111) absent (202) absent (306) absent
 (660) present (280) trace (222) present (303) absent (203) present
 (770) trace (103) present (333) absent (201) present (406) absent

The glancing-angles and interfacial angles measured as described above are shown in the following table. In the case of planes with 'halved spacings' the second order reflection was measured, from which has been calculated the corresponding first order for insertion in the table. The values agree with those calculated from a unit tetragonal cell of dimensions $a = 11.08 \text{ \AA}$. and $c = 9.22 \text{ \AA}$. These values give an axial ratio of 0.835, in good agreement with that crystallographically determined, viz. $c/a = 0.839$.

Plane.	Glancing-angles.		Angle.	Interfacial angles.	
	θ (mean).	θ (calc.).		Mean.	Calc.
(100) ...	1° 49'	1° 50'	(001) : (101) ...	39° 59'	39° 52'
(110) ...	5° 12'	5° 12'	(001) : (201) ...	59° 14'	59° 6'
(140) ...	7° 41'	7° 35'	(001) : (102) ...	22° 45'	22° 40'
(230) ...	6° 43'	6° 33'	(001) : (203) ...	29° 1'	29° 1'
(180) ...	5° 51'	5° 49'	(001) : (103) ...	15° 34'	15° 33'
(001) ...	2° 11'	2° 12'	(100) : (110) ...	45° 6'	45° 0'
(111) ...	3° 9'	3° 25'	(100) : (140) ...	75° 53'	75° 58'
(221) ...	5° 52'	5° 40'	(100) : (230) ...	56° 15'	56° 19'
(101) ...	2° 50'	2° 52'	(100) : (130) ...	71° 85'	71° 84'
(201) ...	4° 17'	4° 17'	(001) : (111) ...	49° 25'	49° 45'
(102) ...	4° 53'	4° 48'	(001) : (221) ...	66° 45'	67° 3'
(203) ...	7° 36'	7° 34'			
(103) ...	6° 55'	6° 54'			

¹ G. Greenwood, Min. Mag., 1925, vol. 20, p. 897.

The density of the crystal was found to be 1.838, and calculation thus proves that there are eight molecules in the unit. An examination of the table of results shows that the following planes possess 'halved spacings': (100), (001), (111), and (221). By small calculations of the type described above we see that the space-groups in the ditetragonal alternating class which have the (100) spacing halved are all those from V_d^3 to V_d^{12} . Further calculation using the (230) planes shows that those which possess (100) halved and (230) normal, like the crystal

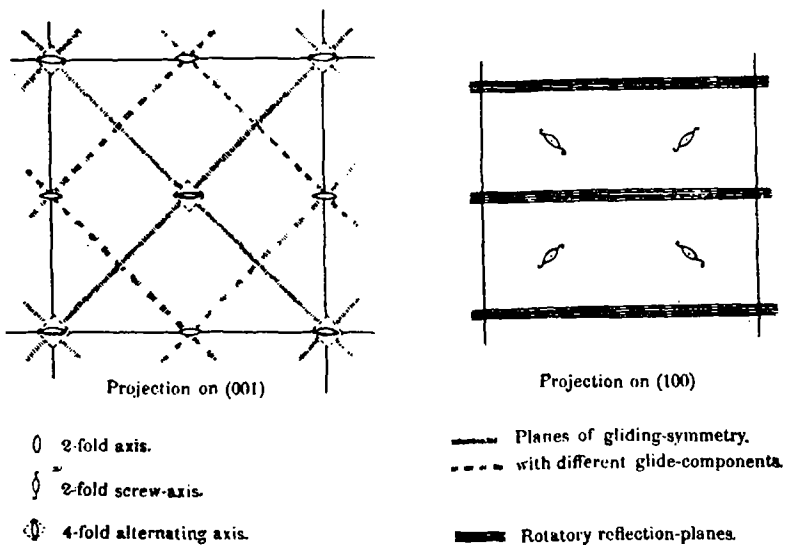


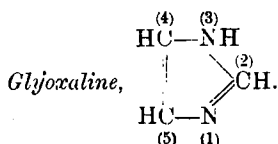
FIG. 1. Symmetry of the space-group V_d^4 of Glyoxaline-4-sulphonic acid.

in question, are only V_d^3 and V_d^4 . To decide between these two we may use the planes (001). And we find that the only group which gives (100) and (001) halved together with (230) normal is V_d^4 . Hence this is the space-group for the crystalline structure of glyoxaline-4-sulphonic acid. A similar result is obtained by using the tables of W. T. Astbury and K. Yardley,¹ where this space-group [D_{2h}^4] is described as having ' {100} halved', and ' { $h h l$ } halved if l is odd'; all others being normal. The fact that eight molecules occur in the unit shows that the crystal-molecule must be completely asymmetric. Since in the previous determination of the crystal-class of this substance, the only evidence was

¹ *loc. cit.*, p. 238.

the alternating occurrence of small facets, this point should be given further consideration. The whole of the other space-groups in the tetragonal system were examined and found not to give the required spacings, whatever the number of molecules in the cell. In those cases where the choice of crystal-axes was arbitrary—sometimes a rotation of 45° round the c -axis can be made, bringing (110) to (100), &c.—the alternative orientation was considered and found never to fit. It might be remarked that such a second orientation is not possible in the ditetragonal alternating class. This definitely fixes the crystal-class and the space-group.

The elements of symmetry of the space-group V_d^4 are shown in fig. 1, in which is represented a projection of the planes (001) and (100). There are planes of rotatory reflection parallel to (001) at a distance c/a apart. Parallel to the c -direction in the crystal are tetragonal axes of the second order passing through the vertical edges and middle of the cell, also digonal rotation-axes through the mid-points of the horizontal edges of the cell. The planes (110) are planes of gliding-symmetry; they are of two kinds, having different glide-components. There are digonal screw-axes parallel to [100] (and also [010]) at a distance $a/4$ and $c/4$ from the sides and base of the cell.



In the case of this substance the task was much more difficult. No crystallographic examination had been or could be made, since the crystals were always so unsatisfactory. Many attempts were made to grow crystals. The substance had a great tendency to crystallize as long and rather fibrous prisms, having no terminal faces. After experiments with many solvents it was found that the best crystals were obtained by crystallization from ether, and that the prismatic habit was most pronounced when grown from benzene solution. In this latter case, prisms 50 mm. in length and less than 1 mm. in thickness were usually obtained. The first zone to be investigated was the prism-zone. This zone was found to contain a face (100), together with prism-faces of the type $(h \bar{k} 0)$ and $(h \bar{k} 0)$. This can only be explained by the crystal being orthorhombic or monoclinic. By suitable re-setting on the wax of the holder a second zone, containing again (100) and passing over the

broken ends of the crystal, was brought into position. No face could be found at right angles to the face (100). All the angles measured between the crystalline planes justified the reference of these planes to two axes obliquely inclined to each other, and lying in the plane at right angles to the zone-axis. By measuring the angle between two faces, one in each zone, it is possible to find the angle between the two zones. This was found, as expected, to be 90° . A stereographic projection of these zones and crystal-angles showed that the crystals are monoclinic. In the following table are recorded the glancing-angles and the crystal-angles, which lead to a unit monoclinic cell of dimensions $a = 7.67 \text{ \AA}$., $b = 5.44 \text{ \AA}$., $c = 5.12 \text{ \AA}$., and $\beta = 63^\circ 11'$. This gives an axial ratio of $a : b : c = 1.411 : 1 : 0.942$. All the glancing-angles are found to agree with those calculated from this unit-cell, i.e. none of the spacings are halved.

Plane.	Glancing-angles.		Interfacial angles.		
	θ (mean).	θ (calc.).	Angle.	Mean.	Calc.
(100) ...	$2^\circ 59'$	$2^\circ 58'$	(100) : (810) ...	$22^\circ 51'$	$22^\circ 45'$
(110) ...	$4^\circ 47'$	$4^\circ 47'$	(100) : (210) ...	$32^\circ 24'$	$32^\circ 10'$
(210) ...	$6^\circ 58'$	$7^\circ 2'$	(100) : (320) ...	$40^\circ 4'$	$39^\circ 59'$
(120) ...	$8^\circ 5'$	$8^\circ 2'$	(100) : (110) ...	$51^\circ 31'$	$51^\circ 31'$
(180) ...	$11^\circ 44'$	$11^\circ 42'$	(100) : (120) ...	$68^\circ 30'$	$68^\circ 20'$
(810) ...	$9^\circ 39'$	$9^\circ 41'$	(100) : (130) ...	$75^\circ 16'$	$75^\circ 10'$
(320) ...	$11^\circ 42'$	$11^\circ 42'$	(100) : (201) ...	$27^\circ 32'$	$27^\circ 29'$
(201) ...	$9^\circ 8'$	$8^\circ 55'$	(100) : (101) ...	$39^\circ 4'$	$39^\circ 29'$
(101) ...	$6^\circ 39'$	$6^\circ 23'$	(100) : (001) ...	$63^\circ 11'$	$63^\circ 11'$
(001) ...	$4^\circ 28'$	$4^\circ 28'$	(100) : ($\bar{1}02$) ...	$80^\circ 56'$	$81^\circ 24'$
($\bar{1}02$) ...	$8^\circ 29'$	$8^\circ 2'$	(100) : ($\bar{1}01$) ...	$101^\circ 28'$	$101^\circ 28'$
($\bar{1}01$) ...	$4^\circ 14'$	$4^\circ 6'$	(100) : (201) ...	$132^\circ 43'$	$132^\circ 21'$
(201) ...	$5^\circ 39'$	$5^\circ 36'$	(110) : (001) ...	$73^\circ 21'$	$73^\circ 42'$

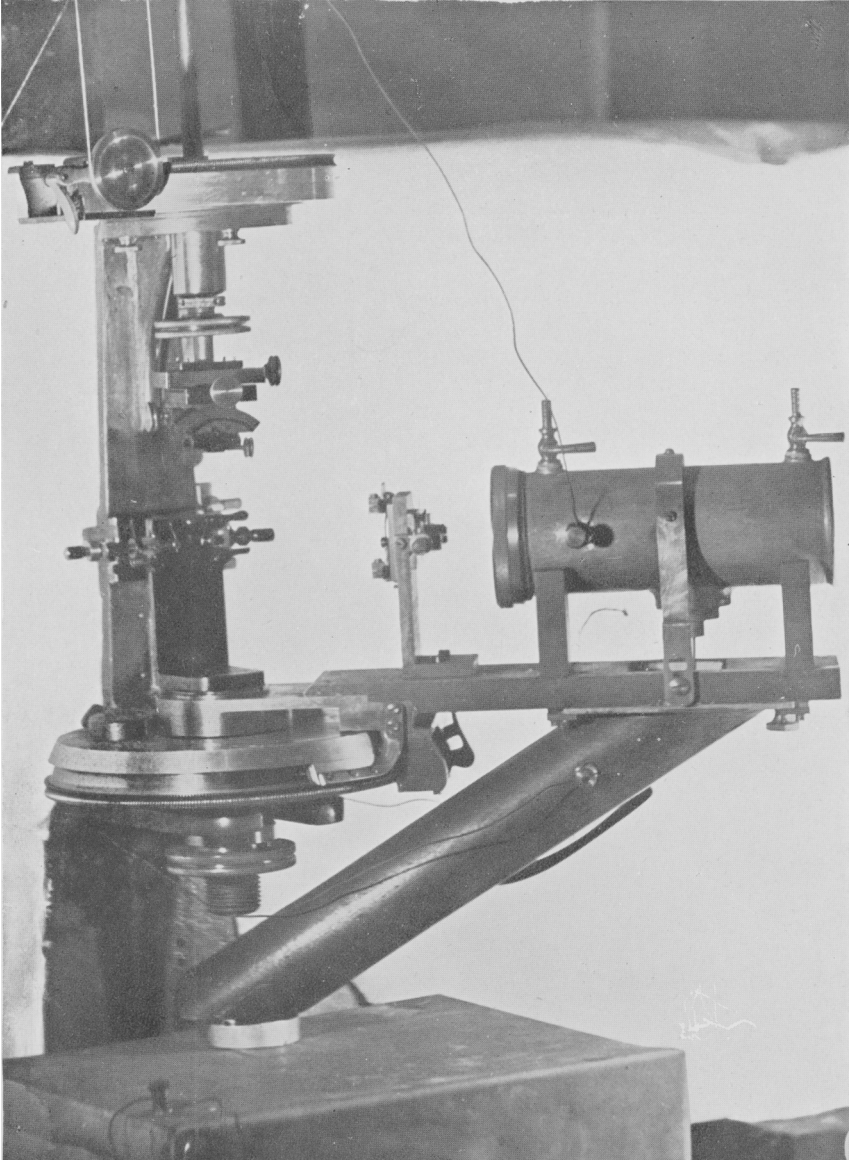
A determination of the density of glyoxaline was made and found to be 1.167. Calculation therefore shows that there are two molecules in the unit-cell. The fact that none of the spacings examined are halved proves that the space-group of the structure must be C_s^1 or C_2^1 or C_{2h}^1 . Each of these space-groups belongs to a different class of the monoclinic system, and it is thus in this case not possible to decide the crystal-class by means of X-ray measurements. Owing to the peculiarly bad manner in which the substance crystallizes it is also impossible to obtain any evidence on this point by the usual crystallographic methods. By considering from the space-group point of view the fact that there are two molecules in the unit, we see that if the crystal is holohedral, the glyoxaline molecule itself must possess an element of symmetry—a twofold

digonal axis or a plane of symmetry—whilst if the crystal belongs to either of the two other classes, the molecule must be asymmetric. As ordinarily depicted (see p. 7) the molecule appears asymmetric, but it is a well-known and striking chemical fact that the same substance is obtained by substituting another group for the hydrogen in either the 4 or the 5 positions. Or, in other words, the two nitrogen atoms are quite identical, the hydrogen belonging equally to the two. In view of this fact it is easy to conceive the glyoxaline molecule as possessing a plane of symmetry. It therefore seems likely that the substance crystallizes in the holohedral class and that the space-group concerned is C_{2h}^1 . A description of the symmetry properties of the three space-groups concerned can be found in Niggli's book, pages 146, 150, and 153.

When this work was practically completed Professor F. L. Pyman and his assistants, who have most kindly supplied me with the crystals, were able to obtain rather better crystals of glyoxaline, which showed a face on the end of the prism. These crystals were only obtained once, and it has not been found possible to reproduce them. Using these crystals it was possible to make one or two goniometric measurements, the results of which are shown in the table.

Angle.	Optical goniometer measurement.	X-ray goniometer measurement.
(110) : ($\bar{1}10$)	... 76° 59'	... 76° 58'
(100) : (001)	... 63° 6'	... 63° 11'
(110) : (001)	... 73° 21'	... 73° 21'

Finally I wish to express my best thanks to Professor W. L. Bragg for his many helpful suggestions and advice during this work. I should also like to record my appreciation of the work of Mr. W. Reynolds of the Physics Department workshop, who constructed the actual instrument as well as supplying useful advice on certain practical details.



G. GREENWOOD : X-RAY GONIOMETER