COMMUNICATIONS FROM THE CRYSTALLOGRAPHIC LABORATORY OF THE UNIVERSITY OF MANCHESTER, No. 3.

Crystallographic data for some organic compounds.

By GILBERT GREENWOOD, M.Sc.
John Harling Fellow in the University.

[Read March 17, 1925.]

THE isomorphous relationships for organic compounds are not so simple as they sometimes are for inorganic. Very often a series of chemically similar organic substances does not show any apparent trace of crystallographic similarity. It appears that the introduction of further groups into the molecule may cause the crystal-system to change in a manner which cannot be predicted. Thus, glyoxaline-4(or 5)-sulphonic acid is tetragonal, whilst 4(or 5)-bromoglyoxaline-5(or 4)-sulphonic acid is monoclinic; the introduction of a methyl group into the 2 position gives rise to an orthorhombic crystal, whilst the introduction of the same group into the 1 position leaves the crystal-system unchanged. In some cases it has been found that even though the crystal-system is changed, there still remains a very close similarity between corresponding angles in the different substances. An examination of the crystal-angles of the glyoxaline derivatives shows no such effect in this series. On the other hand, the addition of a methyl group to menthyl bromomethylenephenylhydrazone carboxylate, giving rise to the corresponding *p*-tolyl compound, causes very little change in the axial ratios and crystal-angles. Now it is known that in organic crystals the molecule has a more individual existence than in inorganic crystals. Thus it would seem that in substances of this type if the molecular change is comparatively small the structures remain similar, but if the molecular change is greater there is a more complete change. This is in contrast to an inorganic type of structure where a relatively large change, e. g. K_2SO_4 and Rb_2SO_4, produces an isomorphous crystal.

During the last fifteen years a method of crystallo-chemical analysis

has been developed by E. S. Fedorov. A description of this new method for the identification of chemical substances and an account of its advantages has been given by T. V. Barker.[1] The first essential is that the crystal should have been already examined crystallographically and its characteristics been put on record. In the course of the last eighteen months various crystals have been measured in this laboratory, and their constants are here recorded for future use.

The Menthyl Derivatives.

These two substances were prepared according to the method of A. Lapworth.[2]

Menthyl bromomethylenephenylhydrazone carboxylate.

$C_6H_5 . NH . N : CBr . COOC_{10}H_{19}$. Melting-point 133–134° C.

System.—Orthorhombic, probably holoaxial class (see below, p. 396).

Axial ratios.—$a : b : c = 0{\cdot}923 : 1 : 0{\cdot}641$.

Angle.	No.	Limits.	Mean Obs.	Calc.
(111) : (010)	21	61° 49′–62° 46′	62° 14′	*
(100) : (101)	23	54 49 –55 47	55 12	*
(100) : (110)	12	41 57 –42 42	42 27	42° 41′
(100) : (111)	4	59 35 –59 55	59 44	59 40
(100) : (201)	1	– –	35 43	35 44
(100) : (502)	1	– –	29 44	29 55

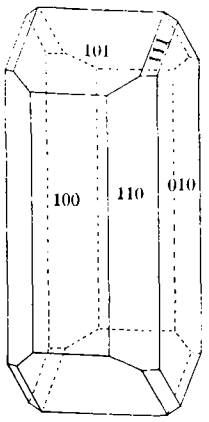


Fig. 1. Crystal of Menthyl bromomethylenephenylhydrazone carboxylate.

Forms and Habit.—The crystals are all small and colourless, and crystallize in one habit (fig. 1). The largest face is (010). The forms {101}, {110}, and {100} are well developed. The forms {111} and {$\bar{1}$11} are usually present as narrow faces, and the more complicated forms {502} and {201} were also observed.

Cleavage.—Good parallel to (001).

Optics.—The acute bisectrix is the axis *b*, and the optic axial plane is (001). Double refraction is strong and positive. The appearance of the

[1] T. V. Barker, Annual Reports of the Chemical Society, London, 1914, vol. 10 (for 1913), p. 247; 1915, vol. 11 (for 1914), p. 248; Chem. News, 1912, vol. 106, p. 199; The Lancet, 1917, vol. 1 (for 1917), p. 278; Min. Abstr., 1923, vol. 2, p. 100.

[2] A. Lapworth, Journ. Chem. Soc. London, 1903, Trans. vol. 83, p. 1114.

interference-figure in white light suggests crossed axial dispersion (cf. A. Lapworth, loc. cit., p. 1127). Measurements of the optic axial angle at about 20° C. show, however, that the axial plane is unchanged between the wave-lengths $\lambda = 671$ and $\lambda = 505$ $\mu\mu$, though the dispersion is very great. The following results were obtained:

Wave-length	671(Li).	589(Na).	546(Hg).	535(Tl).	530.	520.	505$\mu\mu$.
2E	17° 53′	54° 30′	74° 49′	80° 20′	81° 31′	90° 8′	100° 43′

The angle decreases slightly with rise of temperature, as shown by the following measurements obtained in sodium-light on another crystal:

Temperature	18°.	38°.	44°C.
$2E_{Na}$	55° 42′	51° 49′	49° 50′

Menthyl bromomethylene-p-tolylhydrazone carboxylate.

$CH_3 . C_6H_4 . NH . N : CBr . COOC_{10}H_{19}$. Melting-point 155–156° C.

System.—Orthorhombic holoaxial.

Axial ratios.—$a : b : c = 0{\cdot}927 : 1 : 0{\cdot}640$.

Angle.	No.	Limits.	Mean Obs.	Calc.
(100) : (101)	12	55° 8′–55° 46′	55° 23′	*
(100) : (111)	19	59 34–60 18	59 30	*
(111) : (110)	23	46 0–47 0	46 31	46° 43′
(010) : (110)	12	46 55–47 8	47 1	47 8
(110) : (210)	3	17 55–17 58	17 57	17 58

Forms and Habit.—The crystals are yellow in colour. Their habit is prismatic with elongation along the *b*-axis (fig. 2). The predominating form is {100}, and faces of the form {101} are fairly large. The holoaxial character is shown by the relative sizes of the faces of {111} and {$\bar{1}$11}. The forms {110}, {210}, and {010} usually occur, though as small faces.

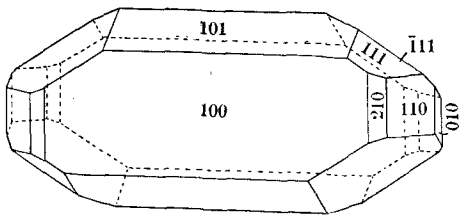


FIG. 2. Crystal of Menthyl bromomethylene-*p*-tolylhydrazone carboxylate.

Cleavage.—Fairly good parallel to (001) and also to (100).

Optics.—The acute bisectrix is the axis *b* and the optic axial plane is (001). Double refraction is positive and fairly strong. Owing to the poorness of the crystals, an interference-figure was difficult to observe, but it was finally obtained by immersing a crystal in oil on the Hutchinson universal apparatus. The figure was too poor to allow measurements of optic axial angle, but by examination in different coloured lights the optic

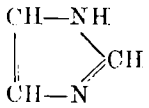
axes were all found to lie in the plane (001). The angle for red is the smallest, and the axial dispersion is strong.

Consideration of the crystal-class of these two substances.—The two substances are optically active in solution. In the *p*-tolyl derivative the hemihedrism of the {111} faces is very evident. Using the colourless phenyl compound, a similar observation was made as with triphenylbismuthine dichloride.[1] An examination of the (010) face in parallel polarized light and crossed nicols showed that in the 'extinction position' the crystal transmitted light of a reddish-brown colour. The explanation of this would appear to be (as in the case of the bismuthine compound) the existence of rotatory polarization and the subsequent transmission of light in the region of the uniaxiality wave-length. The crystals are therefore undoubtedly hemihedral.

The Glyoxaline Compounds.

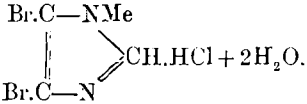
I am greatly indebted to Prof. F. L. Pyman for supplying me with the crystals of these compounds, which have all been prepared in his laboratory by his assistants and himself.

Glyoxaline.



Glyoxaline itself is a substance very difficult to crystallize and even when obtained at its best exhibits only one zone, consisting of long prisms having no terminal faces. It is thus impossible to determine the crystal-system or its axial ratios by the ordinary methods. I am at present attempting to achieve this end by an investigation of its internal symmetry, by means of the X-ray methods. Many of its simple derivatives, e.g., 1-methyl- and 4(5)-bromoglyoxaline are likewise unsuitable for crystallographic measurement. Measureable crystals of 4 : 5-dibromo-1-methylglyoxaline hydrochloride were, however, obtained.

4 : 5-Dibromo-1-methylglyoxaline hydrochloride.[2]



Melting-point when anhydrous 179° C. Density 2·082.

[1] G. Greenwood, Min. Mag., 1923, vol. 20, p. 123.

[2] I. E. Balaban and F. L. Pyman, Journ. Chem. Soc. London, 1924, Trans. vol. 125, p. 1567.

System.—Monoclinic; the faces present indicate holohedral symmetry.
Axial ratios.—$a : b : c = 0{\cdot}897 : 1 : 0{\cdot}653$, $\beta = 82° 12'$.

Angle.	No.	Limits.	Mean Obs.	Calc.
(100) : (110)	17	41° 21′–41° 53′	41° 38′	*
(100) : (011)	11	83 12 –83 38	83 27	*
(110) : (011)	6	63 16 –63 49	63 31	*
(011) : ($\bar{1}$10)	2	73 40 –73 48	73 44	73° 38′

Forms and Habit.—The crystals are colourless. The general habit is shown in fig. 3, though they are often terminated by faces at one end only. The predominating form is {100}; the forms {110} and {011} are well developed; {$\bar{1}$01} is generally present, though the faces are small.

Cleavage.—Fairly good parallel to (010) and (001).

Optics.—The acute bisectrix lies in the plane of symmetry and makes an angle of about −35° with the *c*-axis. The optic axial plane is perpendicular to the symmetry-plane, but horizontal dispersion is not detectable: $\rho < v$. Double refraction is positive and fairly strong.

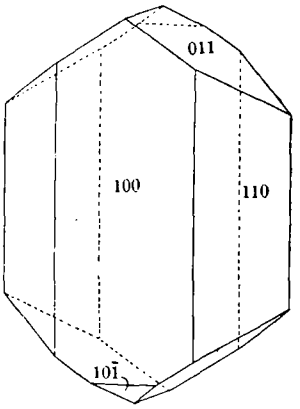
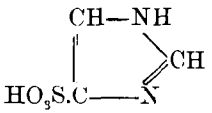


FIG. 3. Crystal of 4 : 5-Dibromo-1-methylglyoxaline hydrochloride.

Glyoxaline-4(5)-sulphonic acid.[1]



Melting-point 307° C. Density 1·838.

System.—Tetragonal; the faces developed indicate ditetragonal alternating symmetry.
Axial ratios.—$a : c = 1 : 0{\cdot}839$.

[1] F. L. Pyman and L. A. Ravald, Journ. Chem. Soc. London, 1920, Trans. vol. 117, p. 1430. The position of the sulphonic acid residue has not been determined with certainty. Compare R. Forsyth, J. A. Moore, and F. L. Pyman, ibid., 1924, vol. 125, p. 919.

Angle.	No.	Limits.	Mean Obs.	Calc.
(001) : (011)	10	39° 44′–40° 28′	40° 0′	*
(100) : (110)	6	44 42–45 37	45 9	45° 0′
(110) : (101)	10	62 20–63 24	62 40	62 58
(110) : (112)	4	58 54–59 51	59 20	59 19

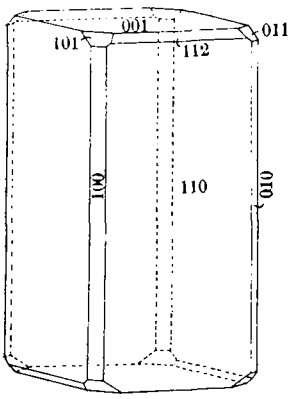


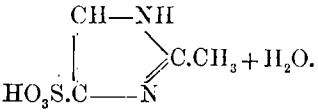
Fig. 4. Crystal of Glyoxaline-4(5)-sulphonic acid.

Forms and Habit.—The crystals usually form colourless rectangular blocks bounded by {110} and {001} (fig. 4). The form {101} is often present as very small triangular facets, whilst the forms {100} and {112} occur only as very narrow strips.

Cleavage.—The crystals are rather fibrous and cleave easily parallel to (110). There is also a cleavage, but less good, parallel to (001).

Optics.—Double refraction is strong and positive. Measurements with a refractometer gave for sodium-light $\epsilon = 1{\cdot}625$ and $\omega = 1{\cdot}551$.

2-Methyl-glyoxaline-4(5)-sulphonic acid.[1]



Melting-point of the dried acid 279° C. Density 1·686.

System.—Monoclinic; faces present indicate the holohedral class.
Axial ratios.—$a : b : c = 0{\cdot}529 : 1 : 0{\cdot}408$, $\beta = 60° 38′$.

Angle.	No.	Limits.	Mean Obs.	Calc.
(010) : (011)	24	70° 0′–70° 46′	70° 25′	*
(010) : (110)	20	65 4–65 22	65 15	*
(110) : (011)	22	55 52–56 17	55 57	*
(110) : (0$\bar{1}$1)	17	73 27–74 3	73 44	73° 47′

[1] R. Forsyth, J. A. Moore, and F. L. Pyman, Journ. Chem. Soc. London, 1924, Trans. vol. 125, p. 921.

Forms and Habit.—The forms {010}, {110}, and {011} are about equally developed, giving rise to crystals of the type of fig. 5. A face (2̄11) has been observed.

Cleavage.—Fairly good parallel to (100).

Optics.—The acute bisectrix lies in the symmetry-plane and makes an angle of about $-71°$ with the c-axis. In white light the crystal shows traces of horizontal dispersion; $\rho < v$. The double refraction is fairly strong and negative. The crystals soon became filled with opaque patches, which made optical investigations very difficult.

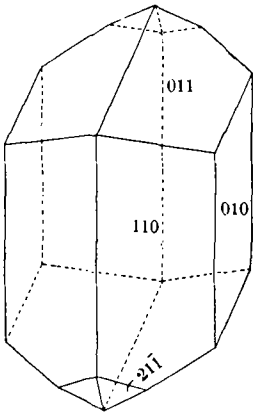
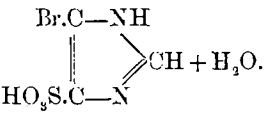


FIG. 5. Crystal of 2-Methyl - glyoxaline-4(5)-sulphonic acid.

4(5)-Bromoglyoxaline-5(4)-sulphonic acid.[1]



Melting-point 280° C., apparently after drying. Density 2·085.

System.—Monoclinic; the faces present indicate holohedral symmetry.
Axial Ratios.—$a : b : c = 0{\cdot}851 : 1 : 0{\cdot}492$, $\beta = 61° 15'$.

Angle.	No.	Limits.	Mean Obs.	Calc.
(001) : (110)	26	67° 6′–67° 42′	67° 20′	*
(010) : (110)	26	52 35 –53 50	53 16	*
(001) : (011)	6	23 12 –23 40	23 21	*
(001) : (100)	3	60 57 –61 10	61 5	61° 15′
(001) : (2̄01)	4	66 15 –66 24	66 20	66 22
(2̄01) : (1̄10)	3	60 44 –60 56	60 48	60 43
(110) : (01 1̄)	5	96 23 –96 42	96 36	96 43

[1] I. E. Balaban and F. L. Pyman, Journ. Chem. Soc. London, 1922, Trans. vol. 121, p. 954.

Forms and Habit.—The crystals are colourless and of the general shape shown in fig. 6. Predominating forms are {001} and {110}. The forms {201} and {011} occur as small facets. The crystals often grow into large flat tablets parallel to the face (110).

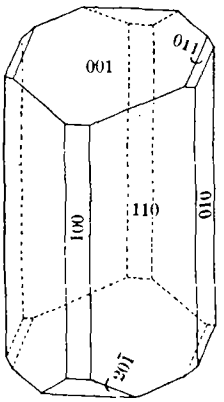
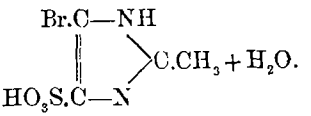


Fig. 6. Crystal of 4(5)-Bromoglyoxaline-5(4)-sulphonic acid.

Cleavage.—Good parallel to (001).

Optics.—The acute bisectrix lies in the symmetry-plane and makes an angle of about $-40°\ 30'$ with the *c*-axis. The optic axial plane is (010); $\rho < v$. Double refraction is strong and negative.

2-Methyl-4(5)-bromoglyoxaline-5(4)-sulphonic acid.[1]



Melting-point 266° C., apparently *not* anhydrous. Density 1·968.

System.—Orthorhombic; the faces present indicate the holohedral class of this system.

Axial ratios.—$a : b : c = 0{\cdot}594 : 1 : 0{\cdot}432$.

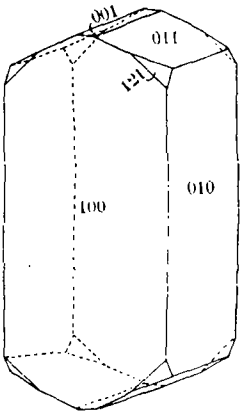


Fig. 7. Crystal of 2-Methyl-4(5)-bromoglyoxaline-5(4)-sulphonic acid.

Angle.	No.	Limits.	Mean Obs.	Calc.
(100) : (121)	44	60° 56′–61° 19′	61° 10′	*
(010) : (011)	47	66 21–67 0	66 38	*
(010) : (121)	33	54 53–55 26	55 7	55° 4′
(011) : (121)	8	33 7–33 18	33 14	33 19

Forms and Habit.—The usual type of crystal is a rectangular prism as shown in fig. 7, consisting of the predominating forms {100} and {010}. The face (010) is really two vicinal faces lying in the zone

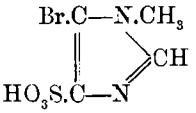
[1] L. Light and F. L. Pyman, Journ. Chem. Soc. London, 1922, Trans. vol. 121, p. 2629.

[100]. Other forms are {011}, {001}, and {121}, the last two being represented by quite small faces.

Cleavage.—Good parallel to (001): also less perfect parallel to (010).

Optics.—The acute bisectrix is the axis *a*, and the axial plane is (010). Double refraction is positive and strong. The dispersion is $\rho > v$.

1-Methyl-5-bromoglyoxaline-4-sulphonic acid.[1]



Melting-point 284° C., after drying. Density 2·186.

Angle.	No.	Limits.	Mean Obs.	Calc.
(010) : (011)	14	61° 35′–61° 41′	61° 38′	*
(110) : (011)	18	67 24–68 0	67 49	*
(110) : (010)	18	46 12–47 7	46 42	*
(110) : (01$\bar{1}$)	22	73 28–74 16	73 56	72° 57′
(110) : (101)	15	65 5–66 53	66 36	66 29
(110) : (12$\bar{1}$)	1	—	44 47	44 42

System.—Monoclinic: the faces present indicate holohedral symmetry.

Axial Ratios.—$a : b : c = 0{\cdot}945 : 1 : 0{\cdot}542$, $\beta = 85° 24'$.

Forms and Habit.—The general type of the crystals, which are colourless, is shown in fig. 8. The predominating form is {110}. Less developed forms are {100} and {010}. The crystals are usually very poor and terminated at one end only. The terminal faces are {011} and {101}. The face (12$\bar{1}$) has been observed.

Cleavage.—The crystal showed no particular cleavages.

Optics.—The acute bisectrix lies in the symmetry-plane, but the crystals were so poor that it was not possible to fix definitely its position. It lies, however, in the acute angle between the *a* and *c* axes. The optic axial plane is per-

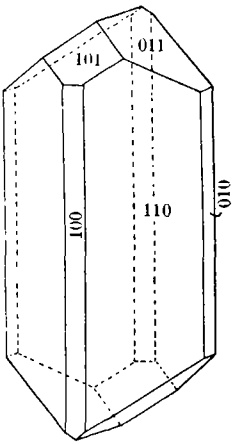


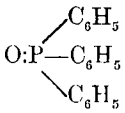
FIG. 8. Crystal of 1-Methyl-5-bromoglyoxaline-4-sulphonic acid.

[1] I. E. Balaban and F. L. Pyman, Journ. Chem. Soc. London, 1924, Trans. vol. 125, p. 1568.

pendicular to the plane of symmetry. Horizontal dispersion is very slight, if even detectable; $\rho > v$. The axial angle is very small. Double refraction is positive and fairly strong.

Miscellaneous Compounds.

Triphenylphosphine oxide.



Melting-point 153° C. Density 1·206.

For the crystals of this substance, which has been prepared many times previously,[1] I am indebted to Drs. F. Challenger and J. F. Wilkinson.

System.—Orthorhombic; the faces present indicate the holohedral class.

Axial ratios.—$a : b : c = 0{\cdot}630 : 1 : 0{\cdot}390$.

Angle.	No.	Limits.	Mean Obs.	Calc.
(010) : (110)	32	57° 40′–57° 59′	57° 47′	*
(211) : (2$\bar{1}\bar{1}$)	16	81 43 –82 21	81 55	*
(110) : (2$\bar{1}\bar{1}$)	7	59 3 –59 13	59 9	59° 12′
(010) : (211)	36	75 58 –76 43	76 18	76 14

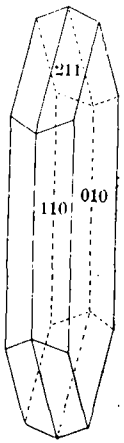


Fig. 9. Crystal of Triphenylphosphine oxide.

Forms and Habit.—The crystals are yellow in colour and usually present a tabular habit as in fig. 9. {010} is the predominating form. The edges of the tablet are bounded by narrow faces consisting of the forms {110} and {211}.

Cleavage.—Fairly good parallel to (201) and (001).

Optics.—The acute bisectrix is the *c*-axis, and the optic axial plane is (010). Double refraction is strong and negative. The dispersion is $\rho > v$.

[1] A. Michaelis and H. v. Soden, Ann. Chem. (Liebig) 1885, vol. 229, p. 306.

p-Tolylazobenzyl formaldoxime.

I am indebted to Dr. T. K. Walker for a supply of the crystals of this new substance, which will shortly be described by him in the Journal of the Chemical Society. Density 1·234.

System.—Monoclinic; the faces present indicate the holohedral class.

Axial ratios.—$a:b:c = 1{\cdot}352:1:1{\cdot}216$, $\beta = 83°\,17'$.

Angle.	No.	Limits.	Mean Obs.	Calc.
(100) : (101)	11	44° 9′–44° 30′	44° 20′	*
(100) : (110)	13	53 9–53 42	53 19	*
(110) : (10$\bar{1}$)	10	67 55–68 34	68 18	*
(100) : (10$\bar{1}$)	17	51 43–52 5	51 50	51° 46′
(110) : (101)	9	64 30–65 7	64 49	64 42

Forms and Habit.—The crystals are red in colour. Habit prismatic as shown in fig. 10. Chief forms are {100}, {101}, and {10$\bar{1}$} in the prismatic zone. Terminal faces are of the form {110}.

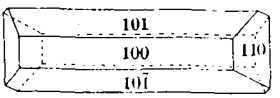


FIG. 10. Crystal of *p*-Tolylazobenzyl formaldoxime

Cleavage.—Good parallel to (010).

Optics.—The acute bisectrix lies in the symmetry-plane and is nearly perpendicular to the face (100). The optic axial plane is perpendicular to the plane of symmetry. The interference-figure exhibits horizontal dispersion very plainly; $\rho > v$. Double refraction is fairly strong and negative.

A fission product of Lupulon.

This substance was also supplied to me by Dr. T. K. Walker, who has isolated it from the degradation products of lupulon, one of the antiseptic principles of hops.[1] It has the formula $C_{18}H_{26}O_4$, and is a yellow substance melting at 91° C. Its exact chemical constitution is yet unknown. Density 1·150.

System.—Orthorhombic; the development of the faces indicates holohedral symmetry,

Axial ratios.—$a:b:c = 0{\cdot}610:1:0{\cdot}701$.

Angle.	No.	Limits.	Mean Obs.	Calc.
(111) : (010)	37	65° 2′–65° 39′	65° 17′	*
(111) : (001)	29	53 3–53 53	53 22	*
(111) : ($\bar{1}$11)	17	86 5–86 46	86 27	86° 28′

[1] T. K. Walker, Journ. Inst. Brewing, 1924, vol. 30, p. 721.

Forms and Habit.—Habit pyramidal as shown in fig. 11. The predominating form is {111}. The form {010} is fairly well developed, whilst the form {001} occurs as small facets.

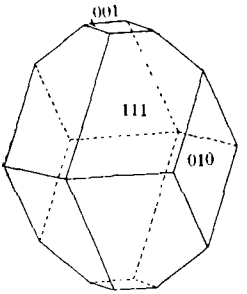
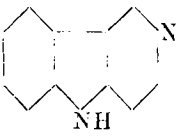


FIG. 11. Crystal of a fission product of lupulon.

Cleavage.—Good parallel to (010), fairly good parallel to (100).

Optics.—The acute bisectrix is the axis *a*, and the optic axial plane is (001). Double refraction is strong and positive. The axial dispersion, $\rho > v$, is also strongly marked.

5-Carboline.



Melting-point 225° C. Density 1·352.

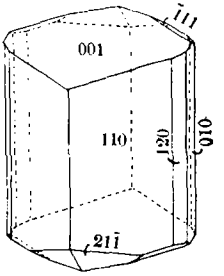


FIG. 12. Crystal of 5-Carboline.

This substance was kindly supplied to me by Prof. R. Robinson and Mr. S. Thornley, by whom it was prepared and described.[1]

System.—Monoclinic; the faces developed indicate holohedral symmetry.

Axial ratios.—$a : b : c = 0{\cdot}8043 : 1 : 0{\cdot}4285$, $\beta = 68° 46'$.

Angle.	No.	Limits.	Mean Obs.	Calc.
(110) : (1$\bar{1}$0)	11	73° 2′–74° 6′	73° 43′	*
(010) : (2$\bar{1}$1)	10	70 55–71 59	71 6	*
($\bar{1}$10) : (2$\bar{1}$1)	8	48 51–49 47	49 28	*
(110) : (001)	25	72 24–73 27	72 53	73° 9′
(010) : ($\bar{1}$11)	2	45 39–45 45	45 42	45 44
(001) : ($\bar{1}$11)	7	37 46–38 39	38 19	38 17
(001) : (2$\bar{1}$1)	6	60 5–60 38	60 25	60 6
(110) : (120)	3	19 2–20 47	19 41	19 27

Forms and Habit.—The crystals are dark in colour. The chief forms are {001} and {110}, as shown in fig. 12. The form {2$\bar{1}$1} is often well

[1] R. Robinson and S. Thornley, Jour. Chem. Soc. London, 1924, Trans. vol. 125, p. 2169.

developed, whilst the forms {010}, {120}, and {$\bar{1}$11} frequently occur, but are only slightly developed. The crystals are often badly formed and distorted.

Cleavage.—None observed.

Optics.—Owing to the dark colour and opacity of the crystals it was found impossible to make an optical examination.