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The Crystal Structure of 6-Amido-3-pyridazone

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The structure of 6-amido-3-pyridazone has been determined by the use of three-dimensional Fourier-series methods, involving successively $|F_o^2|$, F_o and F_o-F_c terms. The unit-cell dimensions are $a = 7{\cdot}55\pm0{\cdot}01$, $b = 12{\cdot}95\pm0{\cdot}02$, $c = 6{\cdot}03\pm0{\cdot}01$ Å, $\beta = 90°\ 5'\pm20'$; the space group is $P2_1/a$ and there are four molecules per unit cell. The structure shows that the molecules, which are practically planar, are bound by hydrogen bonds in layers approximately parallel to $\bar{2}01$. The bond distances C–O 1·25, C–N 1·33 Å in the amido group, are in general agreement with the values found in other amides, the bond C–C = 1·46 Å, linking the amido group to the pyridazone nucleus, is significantly shorter than a single bond; the bond distances of the pyridazone ring are in agreement with its aromatic character. The standard deviation of the bond lengths has been estimated by the method of Booth to be 0·014 Å.

Introduction

The three main features of interest which prompted this analysis of the structure of 6-amido-3-pyridazone were (i) the possibility of tautomeric modifications, (ii) the presence of the amido group, and (iii) the likelihood of hydrogen bonding between the molecules. Only one tautomer of the substance has been isolated chemically, though three tautomeric formulations can be written down. It has been claimed, however, that two tautomers of the related compound 6-methyl-3-pyridazone have been isolated, distinguishable by their infra-red spectra and other physical properties, and the occurrence of stable tautomers of pyridazone derivatives in the solid state therefore appears to be possible (Overend, 1946). In order to distinguish between the tautomers by comparison of bond lengths we therefore undertook an accurate structure analysis, which, it was hoped, would also provide more exact data about the configuration of the amido group than had previously been published. The compound studied was one of a number of pyridazone derivatives prepared by Wiggins, Gregory, Overend & Homer (1948) in the course of work on the synthesis of sulpha drugs from sucrose.

Crystallographic and physical data

The sample, kindly presented by Dr L. F. Wiggins, produced on recrystallization from water a crop of platy crystals, the forms {010}, {$\bar{2}01$} and {001} being the only ones present in the majority of the crystals. There was perfect cleavage parallel to the $\bar{2}01$ face.

6-Amido-3-pyridazone, $C_5H_5N_3O_2$; molecular weight 139; melting point 304°C., with decomposition; refractive indices measured in sodium light, $\alpha = 1{\cdot}41$, perpendicular to $\bar{2}01$, $\beta = 1{\cdot}74$, parallel to b, $\gamma = 1{\cdot}88$; optic axial angle, $2V = 55°$; optically negative; monoclinic; the cell dimensions, measured from rotation photographs were

$$a = 7{\cdot}55\pm0{\cdot}01,\ b = 12{\cdot}95\pm0{\cdot}02,\ c = 6{\cdot}03\pm0{\cdot}01\ \text{Å};$$
$$\beta = 90°5'\pm20'\ (\lambda\ \text{Cu}\ K\alpha = 1{\cdot}541\ \text{Å});$$

four molecules in the unit cell; density, observed and calculated, 1·56 g.cm.$^{-3}$; $0k0$ present only when $k = 2n$, $h0l$ only when $h = 2n$; space group $P2_1/a$.

The determination of the space group extinctions presented some difficulty, since with Cu $K\alpha$ radiation five weak $h0l$ reflexions were recorded with odd h. Acting on a suggestion of Dr D. Rogers, photographs were taken using radiation of different wavelength, to decide whether these reflexions could have been produced by multiple reflexion (Renninger, 1937). If this were the case, the particular odd $h0l$ reflexions obtained with copper radiation would not be present on photographs taken with Fe $K\alpha$ radiation. They were indeed found to be absent, but they could only be accounted for as being caused by the Renninger effect by assuming interactions between reflexions of high order and low intensity. In the course of attempting to establish the space group the statistical distribution and the variance of the intensities were calculated (Howells, Phillips & Rogers, 1950; Wilson, 1951), and it was found that both corresponded more to the hypercentric type (Lipson & Woolfson, 1952) than the centric. This was later explained by the fact that eight of the ten heavier atoms in each molecule were roughly centrosymmetrically related. The value of the variance of the intensities was found to be 3·45, and this, together with the absence of the five forbidden reflexions on the Fe $K\alpha$ photograph, was taken as evidence in favour of $P2_1/a$.

The intensities of the reflexions were measured by visual comparison of the observed intensities with a prepared intensity scale. All the intensities of the reflexions obtainable with copper radiation with the

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crystal rotated about the three principal axes were measured. Those about the *a* and *b* axes were measured from sets of oscillation photographs, those taken with the crystal set about its *c* axis from equi-inclination Weissenberg photographs. The intensities were corrected by the application of polarization, Lorentz, and Cox & Shaw factors in the usual way, the absorption errors being neglected as the crystals were considerably smaller than the optimum size.

Determination of the structure

The high intensity of the reflexion from the $\bar{2}01$ plane and the perfect cleavage and high refractive indices parallel to this plane all indicated a layer structure composed of planar, or nearly planar, molecules arranged in layers parallel to the $\bar{2}01$ plane. This was confirmed by calculating the Patterson–Harker section at $y = \frac{1}{2}b$, which showed two lines of peaks roughly parallel to this plane. Both this section and the rapid decline in intensity of the higher orders of the $\bar{2}01$ reflexion pointed, however, to a slight displacement of the molecules from the plane. A Patterson section in the $\bar{2}01$ plane gave sufficiently exact information as to the orientation and position of the molecules to enable the structure to be refined. The section was interpreted by drawing on a sheet of tracing paper all the intramolecular vectors in the plane of the molecule which would be expected to occur, assuming a planar model for the molecule. The tracing was superposed on a map of the Patterson section and rotated about the origin until each expected peak on the tracing covered a peak on the map; in this way the inclination of the molecule in the plane was found to within a few degrees. On account of the near centrosymmetric nature of the molecule, molecules related by a centre of symmetry will in effect be related by a simple translation and consequently should give rise to a large intermolecular peak on the Patterson section, representing the relative position of the molecular centre and the space-group centre of symmetry. The orientation and size of the molecule indicated the approximate region in which the peak was to be sought; however, two peaks *A* and *B* (Fig. 1) occurred in this region from either of which reasonable structures could be deduced, and both of which yielded equally good preliminary structure factors. In this connection the method of Booth (1948) for finding the position of a planar molecule, once its orientation is known, failed to give the correct result, the failure being due to the dependence of the method on the knowledge of accurate values of individual structure factors, such as could not be obtained by the method of eye estimation; the incorrect position was finally eliminated by the fact that the structure based on it did not refine.

The refinement of the structure proceeded by calculation of Fourier projections on 001, and then by the steepest-descent method (Booth, 1949) in this projection, since the inclination of the molecules to the direction of projection precluded a good resolution of the atoms in the usual two-dimensional Fourier. The refined *x* and *y* coordinates were made the basis for deducing the signs of general structure factors, following the observation of Goldschmidt & Llewellyn (1950), i.e. by assuming a sinusoidal variation of the amplitudes of the sets of structure factors with the same values of $h+2l$ and k when arranged in the order in which they appear on row lines in the reciprocal lattice. In this way a sufficient number of signs of the general structure factors could be determined from the known signs of the $hk0$ terms to permit the calculation of a Fourier section in the $\bar{2}01$ plane in which all the atoms were resolved. Two repetitions of this process, using increasing numbers of calculated signs in each, enabled the signs of all the structure factors to be found. The refinement was then completed by the calculation of lines and sections through the atoms, and by the correction for errors due to finite termination of series by computing the $F_o - F_c$ series along lines and sections and estimating the errors from these by the method of Booth (1946). The largest error was one of 0·04 Å in the coordinate of the oxygen atom in the amido group; the mean error was 0·01 Å.

In the final stages of refinement empirical scattering

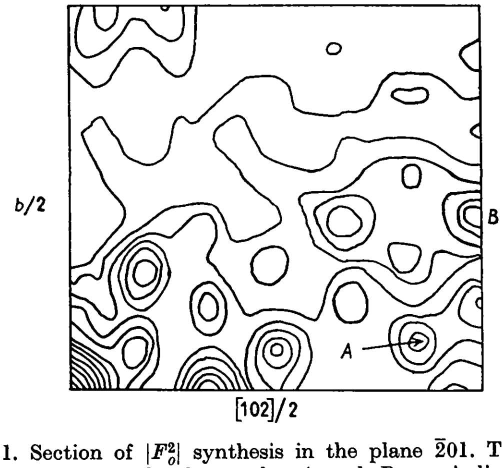

Fig. 1. Section of $|F_0^2|$ synthesis in the plane $\bar{2}01$. The two possible intermolecular peaks *A* and *B* are indicated.

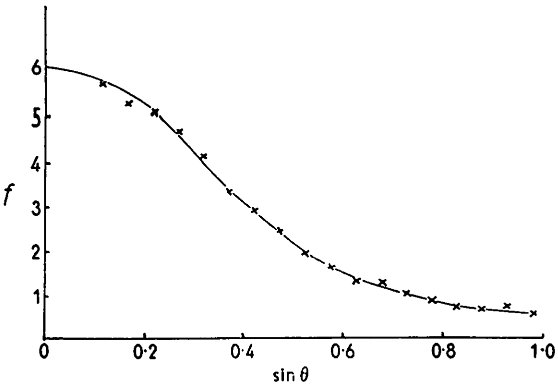

Fig. 2. Empirical scattering factors obtained for this structure.

factors were used, calculated in the following way. The structure factors were divided into groups of approximately constant sin θ and the quotients $\Sigma F_o/\Sigma F_c'$ for each group were plotted against the mean value of sin θ for the group. F_c' denotes the geometrical part of the structure factor, with the oxygen, nitrogen and carbon contributions weighted in the ratio 8:7:6, the hydrogen contributions being neglected. In this way a smooth curve (Fig. 2) was obtained from which the intermediate values of the scattering factors were found by interpolation.

The final value of the discrepancy factor $R = \Sigma|F_o-F_c|\div\Sigma|F_o|$ was 0·22 for a total of 870 structure factors.* The $\bar{2}01$ reflexion, which appeared to be strongly affected by extinction, was included in the evaluation of R; its exclusion lowers R to 0·21. The calculated amplitude of this reflexion was employed in the Fourier syntheses to lessen the errors due to extinction.

Results

Atomic coordinates are given in Table 1. Fig. 3 gives a section of the F_o synthesis in the plane $\bar{2}01$. The molecular dimensions and the arrangements of the molecules are shown in Figs. 4 and 5.

Table 1. *Atomic coordinates*

Atom	x (Å)	y (Å)	z (Å)
C_1	2·23	5·45	3·26
C_2	1·54	6·10	2·18
C_3	1·05	5·36	1·18
C_4	1·10	3·96	1·19
C_5	0·51	3·17	0·12
N_1	2·28	4·08	3·15
N_2	1·73	3·33	2·17
N_3	0·54	1·85	0·22
O_1	2·76	6·02	4·23
O_2	−0·03	3·77	−0·84

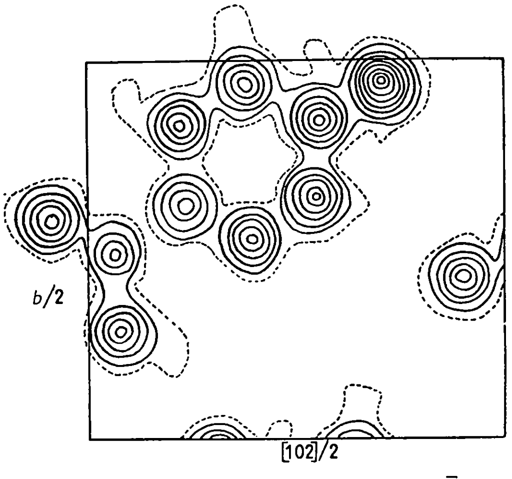

Fig. 3. Section of F_o synthesis in the plane $\bar{2}01$. Contour interval 1 e.Å^{-3}.

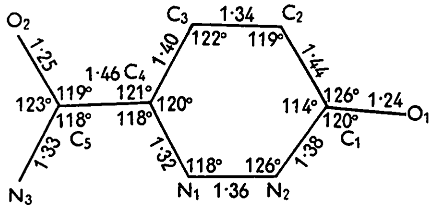

Fig. 4. Dimensions of the molecule.

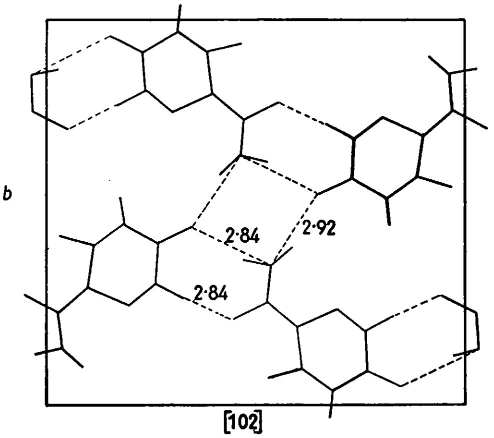

Fig. 5. Arrangement of the molecules in the $\bar{2}01$ plane. Hydrogen bonds are indicated by broken lines.

The molecules are planar within the limits of experimental error, with the exception of the nitrogen and oxygen atoms of the amido group which lie 0·04 and 0·12 Å out of the plane, on opposite sides of it. The plane of the molecule (omitting these two atoms) was found to be

$$z = 1{\cdot}70x + 0{\cdot}11y - 1{\cdot}15$$

by the method of least squares. The coordinates x, y, and z are here expressed in Ångström units.

Accuracy of the results

The probable errors in the coordinates due to random errors in the experimental determination of the structure factors were calculated from the formula given by Booth (1948):

$$\varepsilon_x = \varepsilon_y = \varepsilon_z = \frac{5{\cdot}18}{6\sqrt{V}}\left(\frac{\pi}{\lambda p}\right)^{5/2}\Delta e\,.$$

The probable error in the structure factors, Δe, was taken as the mean of $|F_o-F_c| = 1{\cdot}64$, and the value of p was found to be 4·7 from measurements of the curvature of the peaks. The probable error in the coordinate of a carbon atom was found in this way to be 0·0073 Å, corresponding to a standard deviation of approximately 0·01 Å, and a standard deviation of a bond length of 0·014 Å. The errors due to the finite

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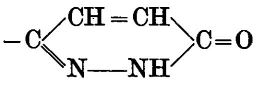
* *Editorial note*.—The table of structure factors, comprising 18 pages of typescript, has been deposited at the Institute of Physics, 47 Belgrave Square, London S.W. 1, England. Application to inspect this table should be made to the Secretary of the Institute.

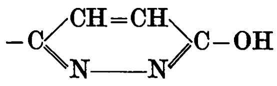
summation of the series were asumed to have been corrected by the difference synthesis.

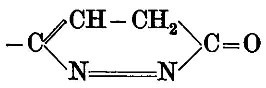
Discussion of the structure

As was expected from the optical and physical evidence, the molecules are arranged in layers nearly parallel to the *b* axis, and to the $\bar{2}01$ plane. The molecules within each layer are knit together by the maximum possible number of hydrogen bonds, but the layers themselves are held together only by van der Waals forces, an arrangement consistent with the easy cleavage parallel to the $\bar{2}01$ plane. The lengths of the hydrogen bonds (2·84 and 2·92 Å) agree with the lengths of these bonds between oxygen and nitrogen atoms as listed by Brown (1951) for a number of compounds. The strong hydrogen bonding accounts also for the high melting point of 304°C.

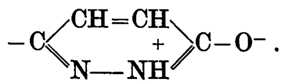
The three tautomeric formulations of the ring part of the molecule which appear possible are


(*a*)


(*b*)


(*c*)

and of these (*c*) may be eliminated because the C_2–C_3 bond is observed to have very nearly the length of a normal C–C double bond, and the N–N bond has an observed length of 1·36 Å corresponding nearly to an N–N single bond, whereas the opposite bond characters would predominate if the structure of the molecule took the form (*c*). The distinction between (*a*) and (*b*) is much more difficult to make, partly because all the bond lengths in the ring, with the exception of those mentioned above, differ significantly from double- or single-bond values, and partly because the distribution of valence bonds in the ring in (*b*) is similar to the distribution in a resonance form of (*a*):



No distinction is possible between the two forms (*a*) and (*b*) according to Hunter (1945), who points out that such cases of tautomerism not involving carbon atoms are accompanied by association in solution. This type of behaviour is shown by some pyridazone compounds and the amides, and the association appears here to persist in the solid state. In the F_o-F_c section in the $\bar{2}01$ plane there are peaks which presumably represent hydrogen atoms; of the hydrogen atoms involved in hydrogen bonding two appear to be attached to the N atom in the amido group, and one to the N_2 atom in the ring; but in addition there are smaller peaks nearer the oxygen atoms which are, however, hardly within the region of significance. In the same way it is impossible to distinguish between the keto and enol forms of the amido group on Hunter's hypothesis. A similar situation exists in the structure of guanine hydrochloride (Broomhead, 1951), where it was also not found possible to differentiate between similar types of tautomers. In the structure of adenine hydrochloride (Cochran, 1951) hydrogen peaks were found in positions indicating that the atoms were attached to particular atoms of the pair forming the hydrogen bonds, but even here there appeared to be a bridge of electron density between the two atoms.

The lengths of the C–O and C–N bonds in the amido group (1·25 and 1·33 Å respectively) agree reasonably well with the lengths of similar bonds in a number of polypeptides and in urea, as listed by Vaughan & Donohue (1952). There is a discrepancy of 0·05 Å in the length of the C–N bond in glutamine and that found by us for that bond, but the difference lies within the combined ranges of experimental error (Cochran & Penfold, 1952). In any case, the bond lengths in 6-amido-3-pyridazone are not strictly comparable with those of any of the other compounds mentioned above because of the conjunction in this compound of an aromatic-type nucleus and the amido group. That the ring part of the molecule has an influence in determining the configuration of the amido grouping is seen from the shortness of the C_4–C_5 bond, which is not paralleled in any of the aliphatic polypeptides of which the structure is known.

It has not been found possible to explain the bond lengths in the molecule as a whole by postulating resonance between a number of simple resonance forms. Similar difficulties were found by Cochran (1951) in attempting to explain the structure of adenine hydrochloride, where again Hunter's form of tautomerism may be expected to occur, and it seems probable that in these circumstances it is not possible to describe the structure in this way.

We are indebted to Dr D. Rogers for a helpful discussion of the space group difficulties and the significance of the statistical intensity data. We are grateful to the University of Birmingham for the provision of a Research Scholarship for one of us (P.C.).

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X-ray Study of Phase Transitions in $PbZrO_3$ Containing Ba or Sr*

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The crystal structures of various phases in (Pb–Ba)ZrO_3 and (Pb–Sr)ZrO_3 systems, the dielectric properties of which were reported previously, have been studied by the powder diffraction method. A crystal structure of a ferroelectric intermediate phase in the (Pb–Ba)ZrO_3 system, which can be observed between the antiferroelectric (tetragonal) and paraelectric (cubic) phases found in pure $PbZrO_3$ when the Ba concentration exceeds 5%, is shown to be a rhombohedral modification of the perovskite structure with α slightly less than 90°. It is shown that, although the (Pb–Ba)ZrO_3 compositions from pure $PbZrO_3$ to (Pb95–Ba5)ZrO_3 do not show this intermediate phase, the application of a strong d.c. field can produce the rhombohedral phase just below their Curie temperatures. A crystal structure of an intermediate antiferroelectric phase in the (Pb–Sr)ZrO_3 system, which begins to appear when the concentration of Sr is as small as 1%, is found to have a tetragonal lattice with c/a slightly less than unity. The observed superlattice lines in this phase are different from those of the antiferroelectric phase in pure $PbZrO_3$.

1. Introduction

A previous investigation (Shirane, 1952) of the dielectric, dilatometric, and calorimetric properties of $PbZrO_3$ containing Ba or Sr has shown the existence of a new intermediate phase besides the antiferroelectric and paraelectric phases found in pure $PbZrO_3$ (Sawaguchi, Shirane & Takagi, 1951). The phase diagrams of the (Pb–Ba)ZrO_3 and (Pb–Sr)ZrO_3 systems determined by the dielectric measurements are shown in Fig. 1. In the (Pb–Ba)ZrO_3 system, the dielectric properties of the intermediate phase are certainly of the ferroelectric type. In the (Pb–Sr)ZrO_3 system, on the other hand, the dielectric response of the intermediate phase can be well explained if we assume this phase to be antiferroelectric, not ferroelectric.

According to Megaw (1946), the crystal structure of $PbZrO_3$ at room temperature is a tetragonal modification of the perovskite structure with $a = 4{\cdot}150$ kX. and $c/a = 0{\cdot}988$. This crystal structure differs from that of ferroelectric $BaTiO_3$ (Megaw, 1946, 1947) in two important respects: first, the axial ratio is less than unity in contrast with the value of 1·01 in $BaTiO_3$, and secondly, some extra lines in addition to the ordinary tetragonal multiplets can be observed. The X-ray analysis of single crystals by Sawaguchi,

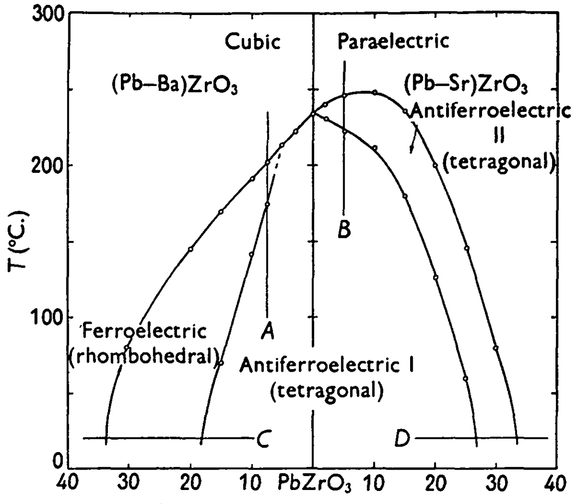

Fig. 1. Phase diagrams of (Pb–Ba)ZrO_3 and (Pb–Sr)ZrO_3 (after Shirane).

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