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# Determination of Elastic Constants of Benzalazine from Thermal Diffuse Scattering of X-rays

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All the nine elastic constants of an orthorhombic single crystal of benzalazine have been determined by photographic methods from the measurements of the intensities of thermal diffuse scattering observed in the Laue photographs taken with monochromatized Cu $K\alpha$ radiation having no higher harmonics. The direct-beam intensity was determined by reducing it by a factor of $10^6$ through absorption in nickel foils of known thickness. The regions of reciprocal space near reciprocal lattice points 602, 022, 002, 600, 710 and 260 were investigated. Corrections were applied to diffusely scattered intensities for general scattering, polarization and skew factors. Corrections for absorption, divergence and second order diffuse scattering were found negligible. The values of elastic constants in units of $10^{10}$ dynes.cm$^{-2}$ are: $c_{11}=41{\cdot}0$, $c_{22}=5{\cdot}2$, $c_{33}=9{\cdot}4$, $c_{44}=0{\cdot}74$, $c_{55}=6{\cdot}70$, $c_{66}=8{\cdot}4$, $c_{12}=12{\cdot}2$, $c_{23}=6{\cdot}6$ and $c_{13}=14{\cdot}6$. The accuracy of the elastic constants is estimated to be within 15%.

## Introduction

The thermal diffuse scattering of X-rays has been successfully used for the determination of the elastic constants of a number of substances (Ramachandran & Wooster, 1951*a*, 1951*b*, Chakraborty and Sen, 1959, Wooster, 1962). This method is suitable for soft substances for which only small crystals are available and requires only a small amount of material. There are two methods available for studying diffuse reflexions; one uses photographic plates and films, the other uses Geiger counters or other ionization or scintillation detectors. In the present paper a specially developed photographic method has been applied to the determination of the elastic constants of an organic crystal of benzalazine, belonging to the orthorhombic system. This particular method was preferred because of its simplicity, and its practicability for studying diffuse scattering due to low values of the thermal wave vector and high angular resolution. Other advantages of the photographic method are that stabilization of the output of the X-rays is not essential and that only very small crystals, which can be easily grown, are required.

## Theory

The intensity of the first order thermal diffuse scattering, $I_d'$, from a crystal of volume $\delta V$, is given in terms of the incident intensity $I_0$, by

$$\frac{I_d'}{I_0}=\varepsilon^2\frac{kT}{\tau^2}|F_o|^2\delta V\frac{\mathbf{Q}^2}{\mathbf{q}^2}K[uvw]_{hkl} \tag{1}$$

Here $k$ is Boltzmann's constant, $\tau$ is the volume of the unit cell, $|F_o|$ is the observed structure factor of the plane ($hkl$), $T$ is the temperature, $\mathbf{Q}$ is the reciprocal lattice vector, $\mathbf{q}$ is the thermal wave vector, $\varepsilon$ is the amplitude scattered by a free electron and is given by Thomson's formula, and

$$K[uvw]_{hkl}=P^2A_{11}^{-1}+Q^2A_{22}^{-1}+\mathrm{R}^2A_{33}^{-1}+2PQA_{12}^{-1}+2PRA_{13}^{-1}+2QRA_{23}^{-1} \tag{2}$$

where $P, Q, R$ and $u,v,w$ are direction cosines of $\mathbf{Q}$ and $\mathbf{q}$ respectively. $A_{ij}^{-1}$ can be written down in terms of elastic constants of the matrix inverse to $A_{ij}$, which for orthorhombic crystals like benzalazine is given by

$$\begin{pmatrix}A_{11}\\A_{22}\\A_{33}\\A_{23}\\A_{31}\\A_{12}\end{pmatrix}=\begin{pmatrix}c_{11}&c_{66}&c_{55}&0&0&0\\c_{66}&c_{22}&c_{44}&0&0&0\\c_{55}&c_{44}&c_{33}&0&0&0\\0&0&0&c_{23}+c_{44}&0&0\\0&0&0&0&c_{13}+c_{55}&0\\0&0&0&0&0&c_{12}+c_{66}\end{pmatrix}\begin{pmatrix}u^2\\v^2\\w^2\\uv\\wu\\uv\end{pmatrix} \tag{3}$$

The value of $\mathbf{q}$ for a particular direction of propagation of the thermal waves is calculated from the known orientation of the crystal with respect to the incident beam. In equation (1) all the terms on the right hand side are known except $K[uvw]_{hkl}$, so that if $I_d'/I_0$ is determined, then $K[uvw]_{hkl}$ can be evaluated and from it the elastic constants.

## Experimental method

Crystals of benzalazine were grown from a solution of this substance in a mixture of chloroform and ethyl alcohol by slow evaporation of the solvent at room temperature (25–35 °C). The crystals generally grow as needles elongated along the $c$ axis, bounded by (110), ($\bar{1}10$) and (010) faces and terminated by (001) faces. A suitable crystal roughly of dimensions $0{\cdot}5\times0{\cdot}5\times0{\cdot}5$ mm$^3$ was selected. The dimensions of the crystal were measured with a powerful travelling microscope and its volume was computed. It was checked by weighing the crystal in a Sartorius Selecta microbalance and hence deducing from it the volume of the crystal from its known density.

In the present investigation Laue photographs were taken in a Unicam universal camera which we converted into a cylindrical camera 10 cm diameter. The cylindrical camera had a collimator of 6·5 cm length. The crystal was mounted on the top of a thin aluminum stick with the help of an adhesive (Durofix) and the whole thing was mounted on the top of the goniometer head with sealing wax. The powder diffraction lines of aluminum in the photographs served the purpose of (*a*) determination of the correct orientation of a particular plane with respect to the incident beam, (*b*) measurement of the camera radius and (*c*) calibration of the angle of diffraction, $\varphi$ in the Laue photographs. The crystal was oriented so that the incident beam made an angle very little different from the Bragg reflexion position of the corresponding plane, because we were interested in small $\mathbf{q}$ values only. After the crystal had been oriented, a Laue photograph was taken, the tube being run at 40 kV, 20 mA (Cu radiation). From the known angles of diffraction for aluminum planes, the distances on the film could be converted into angles of diffraction $\varphi$. Thus by measuring the distance between the aluminum (111) line and a particular spot, the angle between the incident X-ray beam and a particular axis of the crystal could be computed. The distance was measured with the help of a comparator and the orientations thus obtained are believed to be accurate upto 1′.

The experimental arrangement used for taking Laue photographs with monochromatic X-rays is shown in Fig. 1. For monochromatization a plane crystal monochromator with a calcite crystal as reflector was used. A Philips sealed copper tube was used as a source of X-rays. After the crystal had been oriented for a particular diffuse spot and an orientation picture had been taken, the camera was adjusted in the monochromatic beam for recording the diffuse reflexion for intensity measurements. The undeviated incident beam was recorded on the film after reduction in intensity by a factor of about $10^6$ by interposing nickel foils in its path just before the film. The thickness of the nickel absorber is adjusted so that the intensity of the direct beam left over after absorption is nearly equal to the intensity of diffuse reflexion. The X-ray tube was run at 17 kV and 25–30 mA so that $\lambda/2$ is practically, and the higher harmonics totally, absent from the monochromatic beam. Each photograph thus taken contained the diffuse reflexion, the impression of the direct beam and the powder diffraction lines of aluminum. A series of monochromatic pictures was taken making the [001], [010] and [100] crystal axes coincide with the axis of the camera for different orientations of the crystal with respect to the incident beam, so as to study diffuse scattering associated with various suitable reciprocal lattice points. Photographs on either side of the Bragg reflexion position were taken for each reciprocal lattice point, and each photograph was developed in fresh developer at a controlled temperature simultaneously with a separate standard wedge recorded on a piece of film cut from the same sheet of film as used in the monochromatic photograph.

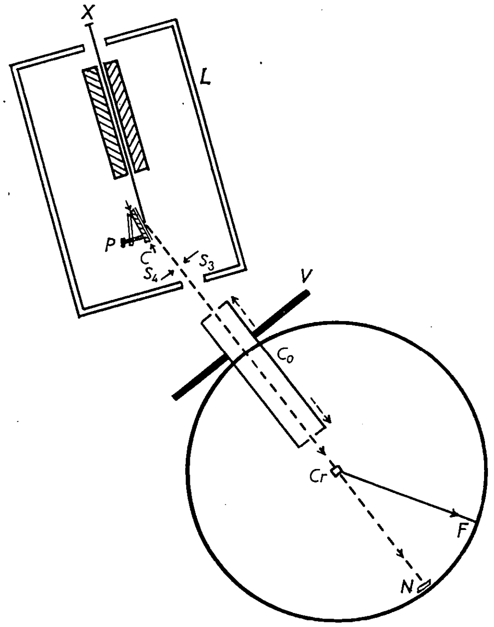


Fig. 1. Schematic diagram of the experimental arrangement for taking Laue photographs with monochromatic radiation. *X* X-ray source, *L* lead shield, *C* calcite crystal, *P* screw, $S_3$, $S_4$ knife edges, *Co* collimator, *Cr* experimental crystal, *F* film, *N* nickel absorber.

For measurement of the intensity distribution of diffuse spots and also the intensity of the direct beam, a Moll recording microphotometer (Kippen Zonen) was used. Since only the diffuse reflexions in the equatorial layer line were considered in the present investigation, the photographs were mounted on the sliding carriage of the photometer in such a way that the scanning spot crossed the middle of the shadow of the crystal in the direct beam impression and the middle of the diffuse spot when the carrigage was moved. The dimensions of the scanning spot were adjusted at 0·02 cm in height and 0·005 in breadth; the current for the illuminating lamp was supplied by 6-volt accumulator batteries and the utmost care was taken to maintain a constant current. The intensities were obtained from the ordinates of the photometric curve by comparison with a standard wedge, following the method of Robinson (1933). The photometric curve for the calibration wedge was recorded under photometric conditions identical with those used for diffuse spots. Intensities of diffuse reflexions and the incident beam thus estimated are on the same arbitrary scale.

Corrections were applied to the measured intensities for general scattering, polarization and skew factors, absorption, divergence and second order diffuse scattering (Wooster 1962). Corrections for absorption, divergence and second order diffuse scattering were found to lie within the limits of accuracy of intensity measurements by the photographic method and were therefore neglected.

## Evaluation of the elastic constants, results and discussion

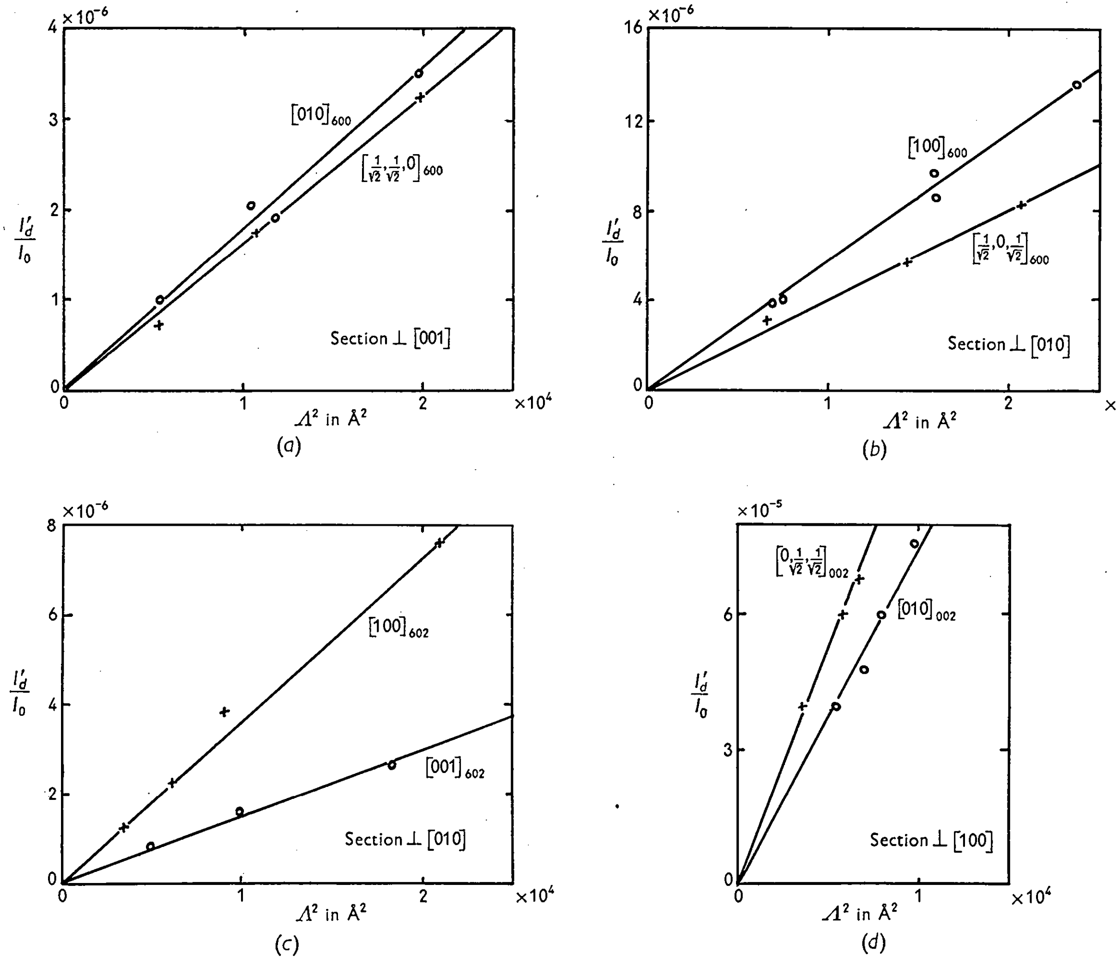
Benzalazine belongs to the space group *Pbcn* and its axial parameters are: $a = 13{\cdot}09$, $b = 11{\cdot}76$ and $c = 7{\cdot}70$ Å. For determining all the elastic constants of this crystal, a series of photographs was taken for 600, 710 and 260 reflexions with the [001] axis vertical; for 600 and 602 with the [010] axis vertical; and for 002 and 022 reflexions with the [100] axis vertical. The structure factor values for these reflexions (Sinha 1961) are presented in Table 1.

The wave vector **q** for any particular direction of propagation of the thermal wave and the corresponding angle of scattering $\varphi$ can be calculated by establishing trigonometrical relations from the consideration of the geometrical position of the circle of reflexion in the reciprocal lattice net for a particular setting of the crystal. The position of the circle is completely determined by the knowledge of the correct orientation of the crystal with respect to the incident beam.

Table 1. *Measured structure factors of some planes of benzalazine studied in this investigation*

| Index of plane | Structure factor |
|---|---|
| 600 | 75·1 |
| 002 | 213·1 |
| 710 | 32·4 |
| 260 | 36·1 |
| 602 | 54·7 |
| 022 | 46·4 |

The intensity corresponding to ordinates of the photometric curve for the diffuse spot is found from the photometric curve of the calibration wedge. The distance between the aluminum 111 peaks in the microphotometer record was calibrated in terms of angle of diffraction. Thus the abscissa of the photometric curve for diffuse reflexion gives $\varphi$ and the corresponding ordinate gives the observed diffuse intensity (uncorrected for any factor) $I_d$. $I_d/I_0$ was



Figs. 2. Variation of intensity of diffuse scattering with the square of the wavelength of thermal waves, $\Lambda^2 = (1/|q|^2)$ for various directions of propagation vector and various reciprocal lattice points.

plotted against $\varphi$ for each case and these curves were used for determining the value of $I_d/I_0$ corresponding to a certain $\varphi$, which corresponded to a certain wave vector. The value of $(\mu/\varrho)$, the mass absorption coefficient of nickel, for estimating $I_0$ was determined in this laboratory with the help of a G. M. Counter Spectrometer for the same foils as were used in the present investigation. The value of $\mu/\varrho$ was found to be $47{\cdot}46\ \text{cm}^{-1}$, whereas that given in *International Tables for X-ray Crystallography* (1962) is $45{\cdot}7\ \text{cm}^{-1}$. Curves showing the realtionship between the intensity of diffuse scattering and the square of the wave length of the thermal waves ($\Lambda^2=1/q^2$) for points lying in different reciprocal lattice planes along particular directions of propagation of the thermal waves through particular nodes have been drawn. A few such curves are shown in Fig. 2. Since $I_d'/I_0$ values have already been corrected for general background and other scatterings, polarization and all other factors, the curves $I_d'/I_0$ versus $\Lambda^2$ are straight lines passing through the origin. From the slopes of these curves the average value of $K[uvw]_{hkl}$ was determined. It is seen that the six constants $c_{11}$, $c_{22}$, $c_{33}$, $c_{44}$, $c_{55}$, and $c_{66}$ may first be determined by suitable choice of an $(hkl)$ plane and the direction of the $\mathbf{q}$ vector. The value of $K[uvw]_{hkl}$ then depends on one or two constants only. After determining these constants $c_{ik}$ for which $i=k$, it is possible to determine the three elastic constants for which $i\neq k$, namely $c_{12}$, $c_{13}$ and $c_{23}$. For example $c_{12}$ can be found from the knowledge of $K[1/\sqrt{2}, 1/\sqrt{2}, 0]_{h00}$ because the following relation holds (Wooster 1962, p. 92):

$$c_{11}(c_{22}+c_{66})+c_{22}c_{66}-2c_{12}c_{66}-c_{12}^2=\frac{2(c_{22}+c_{66})}{K[1/\sqrt{2},\,1/\sqrt{2},\,0]_{h00}}$$

The value of $K[uvw]_{hkl}$, for the wave vector $\mathbf{q}$ having the same direction cosines as reciprocal lattice vector $\mathbf{Q}$ cannot ordinarily be employed for the evaluation of elastic constants. For such wave vectors the geometry of the reflexion is such that even for the smallest angles of misset of the crystal from the Bragg position for which observations were taken, the value of $K[uvw]_{hkl}$ becomes quite high, and therefore the value of $I_d/I_0$ falls to a low value and can hardly be distinguished from the background intensity.

Table 2. *Elastic constants of benzalazine*

| Elastic constant | $K[uvw]_{hkl}$ from which the elastic constant is evaluated | Value of the elastic constant in unit of $10^{10}$ dynes.cm$^{-2}$ |
|---|---|---|
| $c_{11}$ | $K[100]_{602}$ | 41·0 |
| $c_{22}$ | $K[010]_{022}$ | 5·2 |
| $c_{33}$ | $K[001]_{602}$ | 9·4 |
| $c_{44}$ | $K[010]_{002}$ | 0·74 |
| $c_{55}$ | $K[001]_{600}$ | 6·7 |
| $c_{66}$ | $K[010]_{600}$ | 8·4 |
| $c_{12}$ | $K[1/\sqrt{2},1/\sqrt{2},0]_{600}$ | 12·2 |
| $c_{23}$ | $K[0,1/\sqrt{2},1/\sqrt{2}]_{002}$ | 6·6 |
| $c_{13}$ | $K[1/\sqrt{2},0,1/\sqrt{2}]_{600}$ | 14·6 |

The elastic constants of benzalazine are presented in Table 2 and the corresponding $K[uvw]_{hkl}$ from which they were evaluated are also indicated. $K[100]_{260}$ and $K[010]_{710}$ were used only as a check for the value of $c_{66}$, by calculating the $K$ values from the elastic constants and comparing them with the observed $K[100]_{260}$ and $K[010]_{710}$. It is estimated that because of the inherent errors in the measurement of the intensities of diffuse reflexion and the direct beam, use of absorption screens, and the uncertainty in the estimation of correction factors, the absolute values of elastic constants $c_{44}$, $c_{55}$, and $c_{66}$ may have errors up to 10%. The remaining constants, which depend upon the accuracy of other constants because of the process of their evaluation, may be in error up to 15%. The consideration of the values of the elastic constants obtained here yields interesting results if we attempt correlation of elastic data and crystal structure of benzalazine. Benzalazine has a reasonably well defined layer structure, in which the planar benzene rings of a molecule are parallel to each other and the equation of the mean plane of carbon atoms of the molecule is (Sinha 1961)

$$6{\cdot}3331x-16{\cdot}2674y-28{\cdot}4163z=1$$

The binding between the layers is weaker than the binding in those layers. Corresponding to this we find $c_{11}$, which is a measure of resistance to expansion in layers, greater than $c_{22}$ and $c_{33}$, which correspond to separation of the layers.

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