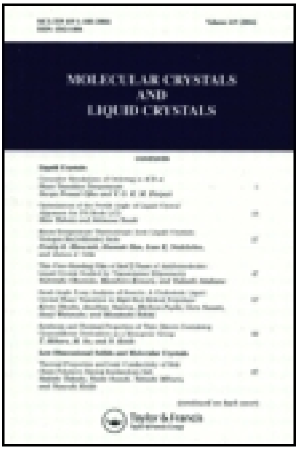

Molecular Crystals and Liquid Crystals

Computer-Assisted Orientation of Low Symmetry Crystals

N. Karl [a] , H. Port [a] & W. Schrof [a]

[a] Physikalisches Institut, Universität Stuttgart, Teil 3, D 7000, Stuttgart-80, Germany

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Computer-Assisted Orientation of Low Symmetry Crystals

N. KARL, H. PORT, and W. SCHROF
Physikalisches Institut, Teil 3, Universität Stuttgart, D 7000 Stuttgart-80, Germany

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Low symmetry organic molecular crystals are oriented by transmission Laue patterns, which are observed "live", and compared with computer-generated diffraction patterns. The technique is applied to anthracene, 1,4-dibromonaphthalene, and β-9,10-dichloroanthracene.

1 INTRODUCTION

The anisotropic properties of low symmetry crystals can only be evaluated from samples which are precisely oriented. Low symmetry frequently occurs in the field of organic molecular crystals (cf. Ref. [1]) leading to difficulties with the orientation of samples which are to be used for such purposes as optical absorption measurements, investigations of electrical conductivity, electron spin resonance, etc.

Low symmetry causes complications with the application of the conventional orientation methods such as polarization optics (conoscopy), Buerger precession photographs, X-ray goniometry or *photographic* Laue technique.

In the present work a method is presented, which is based on transmission Laue patterns *observed "live"*. The lack of abundant symmetry elements in low symmetry crystals and hence in the corresponding diffraction patterns, renders photographic orientation more or less impossible. This problem is solved by direct comparison of Laue patterns, observed continuously on a screen, to the desired one, calculated from a known crystal structure and plotted by a computer.

Most organic compounds contain only low Z-number elements with few electrons; hence the absorption coefficients for X-rays are comparatively small; typical values range about 1 cm^{-1}. Therefore the advantages of the Laue transmission technique, intensive, sharp reflections and directly depicted zone axes, can be utilized.

This paper consists of three parts: First, the experimental techniques are introduced. A description of the computer program follows, which produces the expected Laue pattern with the correct intensity distribution indicated and with the crystallographic axis marked. Finally, examples of some typical applications of the method to different organic crystals are presented.

2 EXPERIMENTAL SET-UP

A collimated X-ray beam from a fine-focus tungsten X-ray tube is used in the conventional way. The direction in which the X-ray goes is designated **X** in what follows. The crystal is mounted on a 3-circle X-ray goniometer head which allows additional x, y, z-motions. The goniometer as a whole can be rotated around a vertical axis V_1 perpendicular to the X-ray beam.

The X-ray reflections are detected by the fluorescence screen of a first image intensifier unit (NYX 2002, Eltro, Heidelberg). The primary beam is absorbed by a small lead cylinder glued to the center of the screen cover. A conical hole, ending in a tiny capillary, serves for depicting a reduced intensity of the primary beam. The weak image on the exit screen of this unit is focussed by a large aperture photocamera lens (Xenoplan 1:1.7/17 mm, Schneider, Bad Kreuznach) onto a second image intensifier (MD 8100, Electrophysics, Nutley, N.J., USA). A high sensitivity video camera (Video 40, LDH 0400/01, equipped with a XQ 1275 Newvicon, Philips, and a Macro Zoomatar 1:2.8/40 lens, Zoomar, Munich) displays the picture on a television screen.

The amplification of the whole system is sufficient to display single event (shot) noise of the first stage. It can be assumed that the main contribution arises from diffusely scattered X-ray intensity; the system therefore approaches the physically reasonable amplification limit.

If precise hard copies are required, the diffraction patterns are photographed in the conventional way after replacement of the first image intensifier stage by a Polaroid® Laue camera.

In addition, a He/Ne laser is mounted on the common optical bench, about 1 m off the crystal, with its beam exactly opposite to the primary X-ray beam. The adjustment is controlled by shining the laser beam through the X-ray collimator. This laser beam, after removal of the electronic image system, can be used to position a natural crystal face, a cleavage plane or an arbitrarily cut and polished surface exactly perpendicular to the laser and hence to the X-ray beam.

3 EXPERIMENTAL PROCEDURE

In our orientation procedure, Laue patterns displayed "live" on a TV screen are successively compared with those calculated and plotted by a computer program. A required orientation is identified when the patterns are identical.

It is useful to adjust the crystal to be oriented, by the aid of the goniometer circles in such a way that the axis V_1 allows rotation about a distinct direct lattice vector. All reflections belonging to the corresponding zone are then depicted on a zone circle which is degenerated to a horizontal straight line through the central image of the primary beam. This line remaines fixed during rotation around V_1. For instance, if the selected vector is the ***monoclinic*** **b**-axis [010], its zone [010], containing all reflections ($h\,0\,l$), is a horizontal line, indicating at the same time the trace of the monoclinic **ac**-plane ($0\,k\,0$) which is a mirror plane in the Laue symmetry and the geometrical locus where the crystallographic **a** and **c** directions have to be searched. By rotation around V_1, the **a** or **c** direction can be positioned parallel to the X-ray beam and hence perpendicular to the projection screen. This situation is recognized by the fact that the corresponding zone circle [$0\ k\ l$] or [$h\ k\ 0$] shrinks and ultimately merges into the primary beam. Distinction between the different [u o w] zones is possible by comparison of the observed with the calculated diffraction pattern.

The orientation of a *triclinic* crystal can only be based on the consideration of the density and intensity distribution of the Laue reflections. A set of calculated maps for successive angular increments are used for this purpose.

A more direct approach to the angular range in question is possible if morphological or optical properties can be used for preorientation, such as natural faces of vapor or solution grown crystals, cleavage planes, sublimation etch pits or optical axes' directions. Using the hollow glass sphere after Waldmann, the latter can be viewed even if the sample is not a plane parallel slice but rather an arbitrary formed fragment.

If radiation damage may cause problems, it is advisable to expose only portions of the sample which are not subject to the actual physical measurement to the X-rays. Alternatively, radiation damage problems can be avoided if the precise orientation can be determined afterwards.

The orientation procedure described above allows a precision which typically amounts to one degree.

If symmetry elements are present (rotation axes or mirror reflection planes), these symmetry elements can be adjusted with a higher precision up to about 0.1°, using the fact that symmetry-equivalent reflections at characteristic lines must appear with the same intensity. In the computer program to be described below, a superposition of characteristic lines onto the X-ray Bremsspektrum, however, has been neglected.

4 COMPUTER PROGRAM

The calculation of the coordinates and the intensities of the Laue transmission reflections is carried out from a known crystal structure by a Fortran program.† The computer produces a plot of transmission reflections; the intensities of the reflections are indicated by the area of the plotted points.

The program is constructed as a dialogue program. It contains four parts, which serve for data input (1), for calculation of Laue coordinates (2) and intensities (3) and for data output (4).

Part 1 organizes the input of lattice parameters (lengths of axes, lattices angles, coordinates of atoms), experimental parameters (voltage of the X-ray tube, distance from projection plane to sample, area to be plotted, the Miller indices of the crystal plane to be oriented, (i.e. to be finally perpendicular to the X-ray beam), the range of Miller indices which will be regarded by the program, and the direction of axes which shall be designated in the plot. Furthermore, the transformation of the crystal axes' coordinate system into an orthonormal system (ONS) is performed by means of metric tensors.[2] The coordinate system, which describes the geometry of the projection plane and the X-ray beam, is also transformed into ONS. This description bears the advantage that the same indices (h', k', l') can be used to specify a plane and the direction normal to it.

Parts 2, 3 together form a loop, in which a given range of Miller indices is scanned, in order to find the most intensive Laue transmission reflections.

Parts 2 performs the calculation of the coordinates of the Laue reflections. The Miller indices of the reflecting plane are transformed into ONS, the scattering angles are determined, and finally the Laue-coordinates are calculated using spherical trigonometry, cf. Refs. 3 and 4. Reflections which do not lie in the range of transmission or overlap with the finite width of the primary beam are eliminated.

In part 3 the wavelength of the reflection is calculated by Bragg's formula. The spacing between the reflecting planes is computed from Miller indices and lattice parameters. Only reflections of a wavelength contained in the spectrum of the X-ray tube are maintained. The calculation of the structure factors is then a first step for the determination of the scattering intensity. For this purpose the known dependence of the atomic scattering factors on wavelength and scattering angle is taken into account.[5] A number of other parameters enter the calculation of the intensity, such as Lorentz factor, absorption correction, wavelength dependence of primary intensity (Kramers formula), geometrical factors, and eventual higher order reflections. The coordinates, the intensities and the Miller indices of the reflections are stored in a buffer and sorted according to the intensity.

In part 4 the program asks for instructions concerning the output of the Laue data. Numerical data can be printed, Laue patterns can be plotted or the

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† The full program may be found in Ref. 10.

program can be started once again after modification of one or more of the parameters.

Plotting instructions allow the user to choose the output logical unit, the number of reflections to be plotted and to determine the scale of the intensity representation. In addition, the reflections can be labeled with their Miller indices. The directions of axes or an explaining text can be plotted as well.

In summary, the program calculates numerical and graphical Laue forward diffraction patterns including triclinic lattices, which are usually neglected with the Laue technique, because they lack Laue symmetry other than the trivial one, $\bar{1}$. The calculation of the scattering intensities and the possibility of designating axes lying in the plane to be oriented are provided.

5 ILLUSTRATIVE EXAMPLES

In what follows we wish to present three examples arranged in the order of increasing complexity.

Anthracene, which is one of the standard compounds among organic molecular crystals, crystallizes in the monoclinic crystal class 2/m (space group $P2_1/\mathbf{a}$). The lattice parameters at 290 K are:[6]

$$\mathbf{a} = 8.562(6)\ \text{Å}$$
$$\mathbf{b} = 6.038(8)\ \text{Å} \quad \beta = 124.7(1)^\circ$$
$$\mathbf{c} = 11.184(8)\ \text{Å}$$

Laue photographs with the X-ray beam ||**b** and ||**c*** were shown elsewhere.[7] Here we wish to demonstrate the coincidence of the calculated with the experimental pattern for the **c***-direction, Figure 1 †). For exactly positioning **c*** || X-ray the following peculiarities can be used: the (4) reflections of the zone [100] must lie on a straight line through the center; in the zone [010], the angle $2\theta_{(20\bar{1})} = 25.47^\circ$ is 1.5° smaller than $2\theta_{(20\bar{2})} = 27.03^\circ$; $F_{20\bar{1}}$ (obs.) = 53, $F_{20\bar{2}}$ (obs.) = 30, Ref. 6.

1,4-Dibromonaphthalene, crystal class 2/m, space group $P2_1/\mathbf{a}$, is distinguished by very long **a** and **b** axes, whereas **c** is short. The monoclinic angle β is near 90°:[8]

$$\mathbf{a} = 27.230(13)\ \text{Å}$$
$$\mathbf{b} = 16.417(7)\ \text{Å} \quad \beta = 91.95(2)^\circ$$
$$\mathbf{c} = 4.048(2)\ \text{Å}$$

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† In all figures the view direction is from the X-ray tube to the crystal; axes pointing in this direction have *positive* signs. Voltage is always 30 kV. Contrast of the original Laue-photographs has been improved for better reproduction.

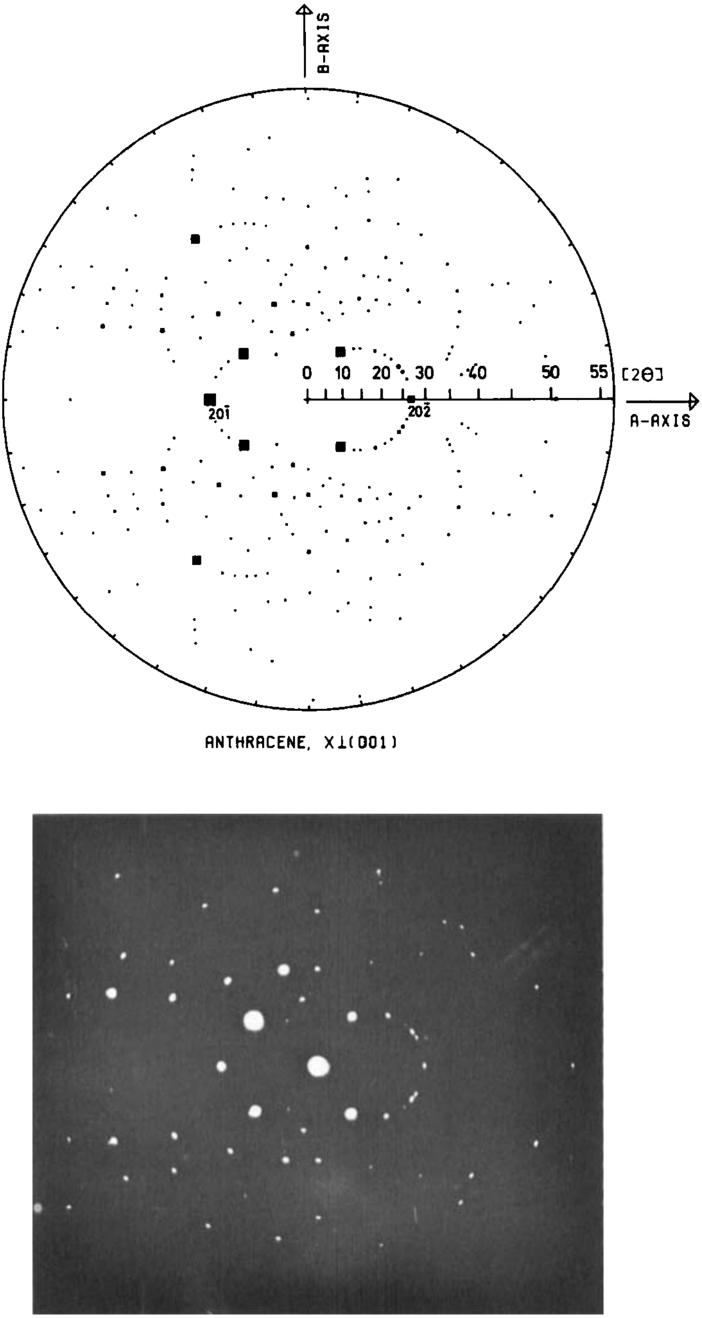

FIGURE 1 Calculated and observed Laue pattern for anthracene, X⊥(001).

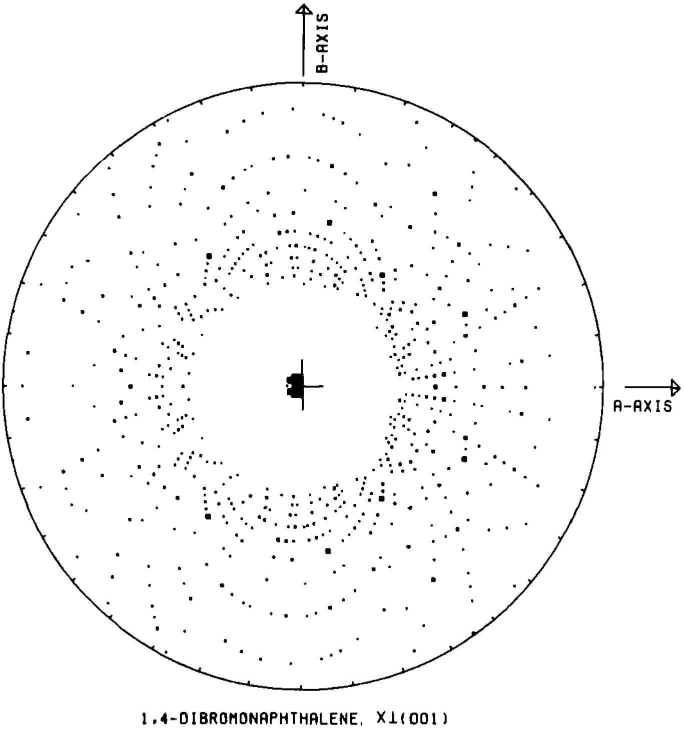

FIGURE 2 Calculated Laue pattern for 1,4-dibromonaphthalene, X⊥(001).

These lattice parameters lead to two helpful consequences for the X-ray beam nearly || **c** or || **c***: (i) A considerable angular range about **c** appears free of reflections. Beyond this gap the reflection abundance is high. (ii) The zone ellipse (~circle) about **c** is visible even for very small scattering angles 2θ (cf. Figure 2†) since $\sin 2\theta = n\lambda/2d$ can be small, because the large **a** and **b** lattice constants lead to large $\mathbf{d}_{hko}$.

Hence, the **c**-direction can be found easily. However, in order to distinguish +**a** from −**a**, comparison with the computer generated pattern is necessary, cf. Figure 3. This situation should be compared with the computer plot for **X**||**c*** which is only 1.9 degrees off **c** (Figure 2).

The ±-**a**-directions have to be searched ~90° off, by rotation around [010], following the trace of the mirror reflection plane in the Laue pattern.

By appropriate rotation of 90° about [100] the **b**-direction can be adjusted || **X**. The zone [001] appears as a straight line with very densely distributed re-

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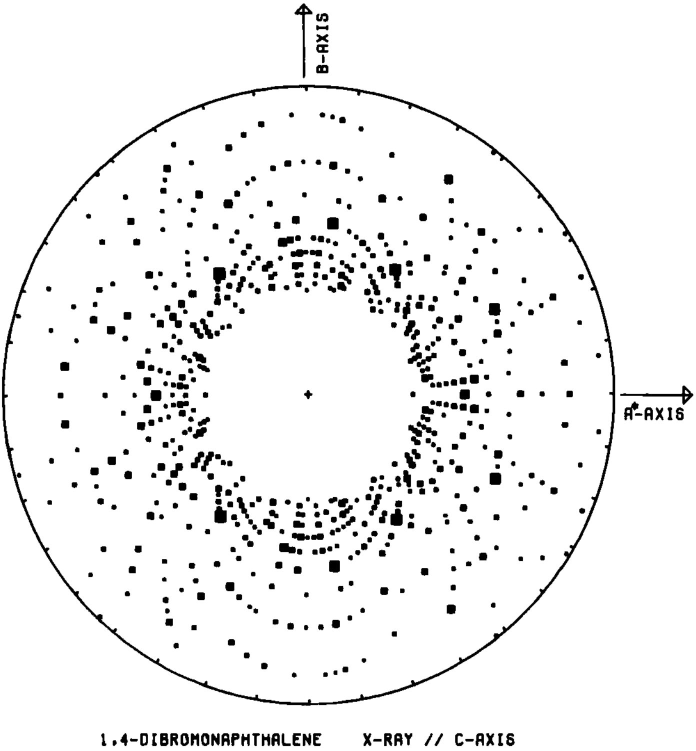
† The calculated relative intensities of the central reflections (*hko*) have been reduced by a factor 0.6 for clarity.



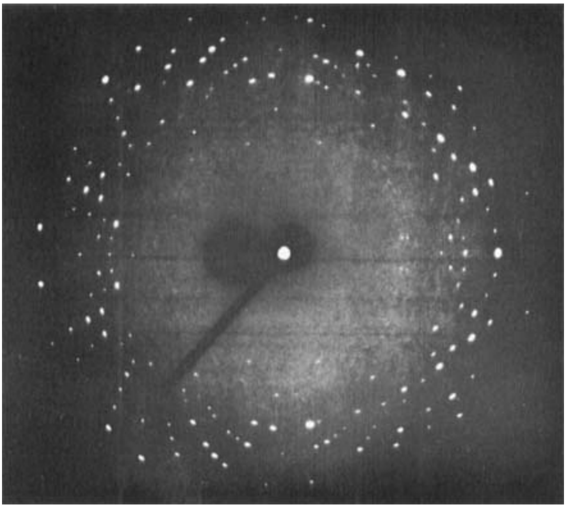
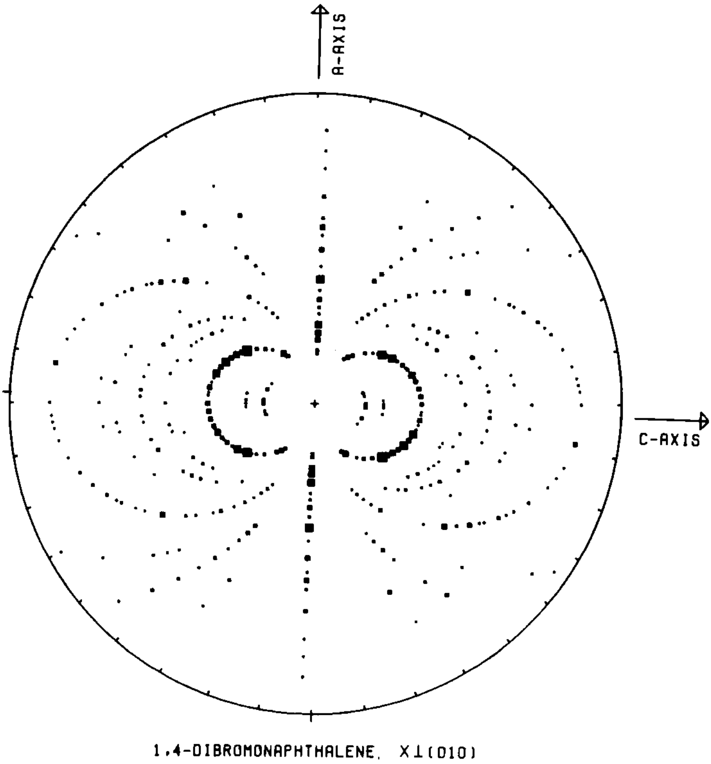


FIGURE 3 Calculated and observed Laue pattern for 1,4-dibromonaphthalene, X||(001).



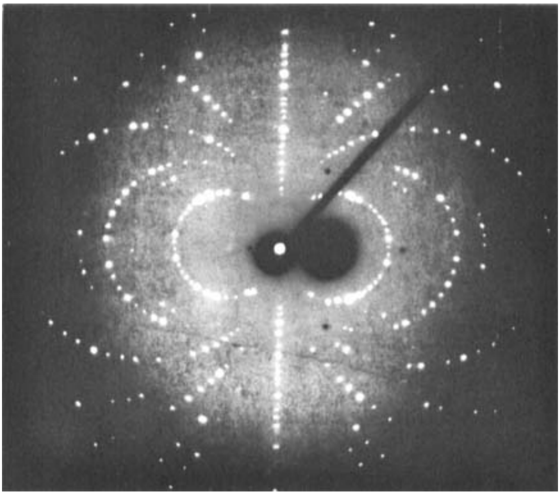
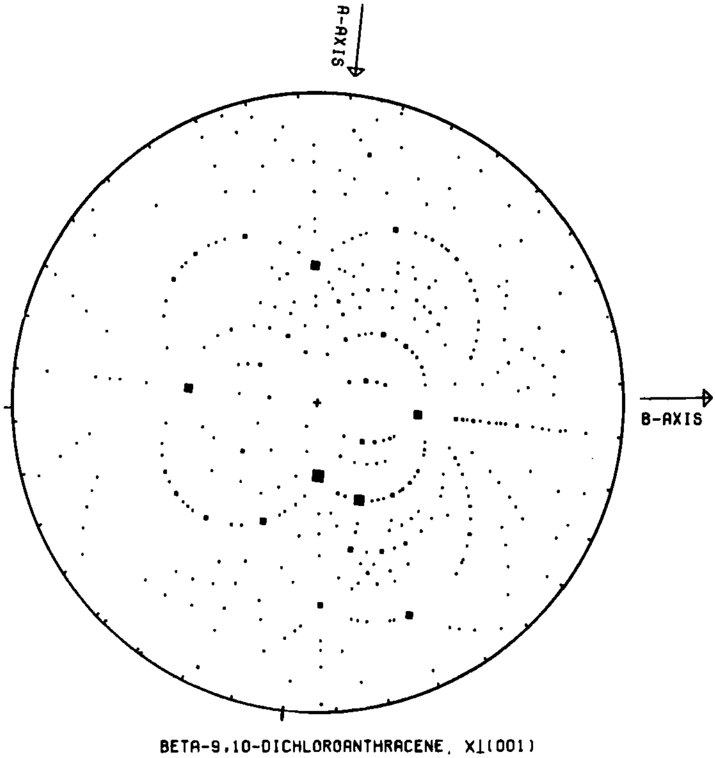


FIGURE 4 Calculated and observed Laue pattern for 1,4-dibromonaphthalene, X⊥(010).



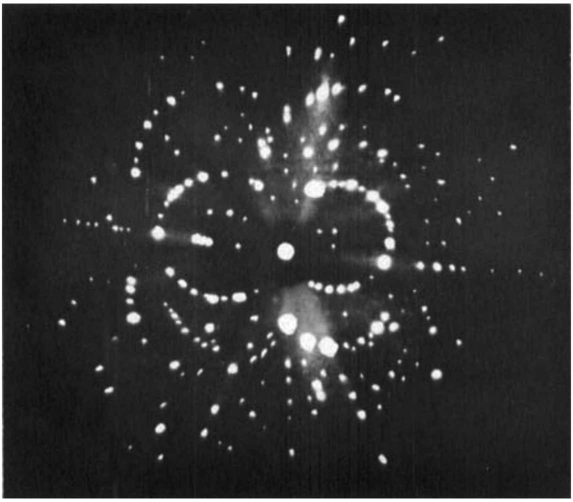


FIGURE 5 Calculated and observed Laue pattern for triclinic β-9,10-dichloroanthracene, X⊥(001).

flections, Figure 4. At a first glance, the figure seems to have the symmetry mm indicating an at least orthorhombic crystal. On close inspection, however, no vertical mirror reflection plane appears. Instead, an angle of 92 degrees can be derived from the photograph. All reflections show inversion symmetry to the center, indicating that a two-fold rotation axis (**b**) in the crystal has been positioned $\parallel$ **X**.

β-9,10-Dichloroanthracene is triclinic, crystal class $\bar{1}$, space group $P\bar{1}$ [9] with the following lattice parameters:

$$\begin{array}{ll} \mathbf{a} = 3.873(2)\ \text{Å} & \alpha = 102.38(2)^\circ \\ \mathbf{b} = 8.585(5)\ \text{Å} & \beta = 95.30(4)^\circ \\ \mathbf{c} = 16.727(7)\ \text{Å} & \gamma = 97.17(3)^\circ \end{array}$$

Since no Laue-symmetry elements other than the trivial one, $\bar{1}$, exist, orientation can only be achieved by comparison of the experimental diffraction pattern with the computed ones. Figure 5 gives an example for the **c***-direction. The relative central angular distances of the strongest reflections can be used to check the precision of the actual orientation.

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