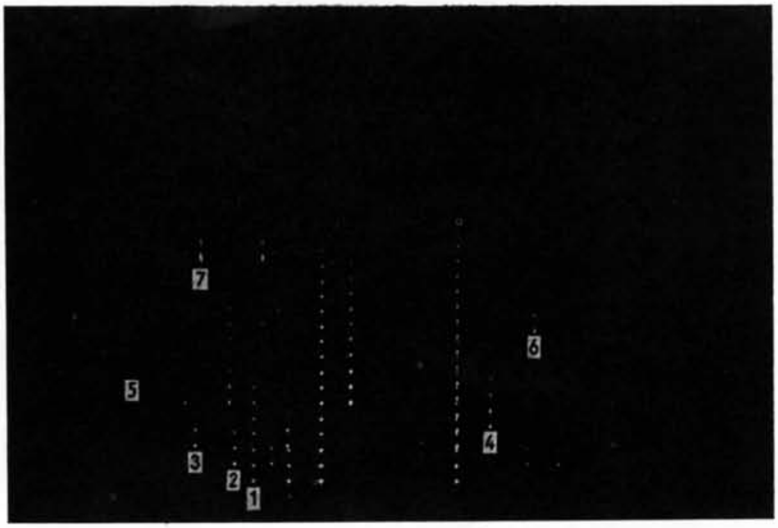

Fig. 1. The strongest film (S_1) of a pack of intensity scales made with a crystal of *i*-erythritol. Cu $K\alpha$ radiation; [100] vertical; 10° oscillation. The numbers indicate a typical scale for each layer line.

from the linear relationship of equation (3), but this example does not involve enough data for this departure to be regarded as significant.

This technique cannot, of course, permit any special solution of the problem of placing intensities on different layer lines on a single scale, though it does provide intensity scales with a larger variety of spot shapes and sizes from which such scaling may be done experimentally with the help of photographs obtained for rotation about different axes. It also provides more consistent data within any one layer, which would be useful if scaling were to be done separately for each layer with the help of a set of calculated structure factors, whether at a late stage in the analysis to improve the final accuracy (Wheatley, 1954), or at the outset on the basis of a 'possible structure' (Grenville-Wells, to be published). As such a scale takes no longer to prepare than the usual zero-layer intensity scale, there is much to gain and nothing to lose by employing it.

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X-ray study of s-tetrazine.

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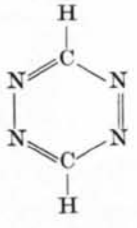
(*Received* 28 *April* 1955)

Tetrazine is a deeply red coloured substance which melts at 99° C. and sublimes easily. It was first prepared by Hantzsch & Lehmann (1900), who proposed a formula which was later shown to be incorrect (Curtius, Darapsky & Müller, 1906) and replaced by the formula:



A close similarity therefore exists between the chemical constitution of tetrazine and benzene, since, theoretically, replacement of four CH groups of the benzene molecule by four isoelectronic nitrogens gives tetrazine.

In view of the above relationship and of the peculiar physicochemical properties of *s*-tetrazine, an X-ray study was undertaken in order to elucidate its crystal and molecular structure. The diffraction intensities were recorded both with a Weissenberg and with a precession camera equipped with a device (Kaufman & Fankuchen, 1949) for cooling the crystal in a stream of cold air to about −20° C. during the exposure.

The unit cell has the dimensions:

$$a = 5{\cdot}23 \pm 0{\cdot}01,\ b = 5{\cdot}79 \pm 0{\cdot}01,\ c = 6{\cdot}63 \pm 0{\cdot}01\ \text{Å};$$
$$\beta = 115{\cdot}30' \pm 15'$$

and contains two molecules.

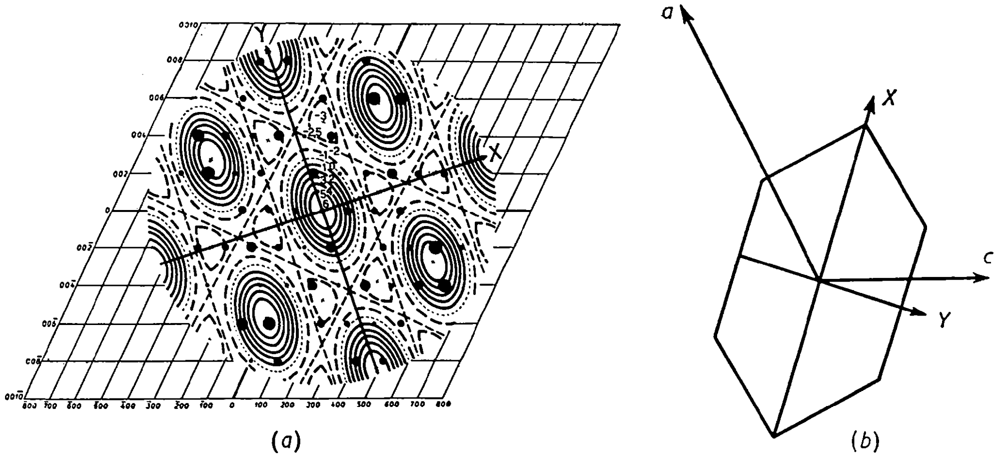


Fig. 1. (*a*) Comparison between a plot of the Fourier transform of benzene and the *h*0*l* weighted reciprocal-lattice section of a tetrazine crystal. (*b*) Approximate orientation of a tetrazine molecule in the unit cell deduced from (*a*).

Since $h0l$ reflexions with $l \neq 2n$, and $0k0$ with $k \neq 2n$ were systematically absent, the space group C_{2h}^5–$P2_1/c$ was chosen. This space group requires four general positions, and therefore a single molecule of *s*-tetrazine must possess a centre of symmetry, in agreement with its chemical formula.

The Fourier-transform method (Ewald, 1935) was used for finding the approximate crystal structure, and hence the signs of the amplitudes for the calculation of a Fourier projection. In view of the close similarity between the chemical formulae of benzene and tetrazine, the Fourier transform of a benzene molecule (Knott, 1940) was applied.

Since the two molecules have the same orientation on $0\bar{1}0$ and lie with their centres at $x = 0$, $z = 0$ and $x = 0$, $z = \frac{1}{2}$, the structure amplitude $F(h0l)$ is directly given by:

$$F(h0l) = \bar{f}T(\xi, \zeta) \times (1+\cos l\pi) = 2\bar{f}T(\xi, \zeta) \quad (\text{for } l = 2n),$$

where $\bar{f}$ is an average atomic scattering factor and $T(\xi, \zeta)$ is the value of the transform at the reciprocal-lattice point $h0l$.

A weighted reciprocal-lattice section was prepared using the $h0l$ intensities recorded on a 30° precession photograph taken with filtered molybdenum radiation. The structure amplitudes derived from the observed intensities were divided by an average scattering factor to which a thermal correction had been applied. The comparison between a plot of the transform and the reciprocal-lattice section was carried out by viewing the transform in a perpendicular direction over the reciprocal-lattice section. The reciprocal-lattice section was tilted with respect to the plane of the transform and the transform was rotated around an axis passing through its origin until a satisfactory agreement was obtained between the values of the transform and those of the weighted amplitudes.

The results are shown in Fig. 1. The *Y* molecular axis makes an angle of about 53° with the 010 plane, while the *X* axis is nearly parallel to this plane. The angle between the *X* axis and the crystallographic *c* axis is about 73°.

The signs of the structure amplitudes directly derived from the Fourier transform were used for the computation of a Fourier projection on 010, which confirmed the predicted picture.

The Fourier-transform method could not be directly applied to the projection on 100 where the two molecules are oriented differently. Inequality relations (Harker & Kasper, 1948) were used for deriving the signs of the largest structure amplitudes. Having observed that the intensities of the $0kl$ reflexions were approximately related by a diad axis at about 45° to the reciprocal axes, it was assumed that the $0kl$ structure amplitudes had the same signs as the $0lk$. On this basis, inequality relations yielded a large number of signs.

A projection on this plane, in spite of the poor resolution, confirmed the orientation of the planar ring deduced from the application of the Fourier-transform method to the 010 projection.

This work is being continued with the aim of measuring bond lengths and bond angles accurately and also in order to determine the electron-density distribution through a refinement process of the present data. It is intended to use for this purpose very low temperatures as it has been observed that a striking resolution of the projections can be obtained by this technique.

We are indebted to Dr G. Settimj for the preparation of *s*-tetrazine.

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