

Acta Cryst. (1963). **16**, 851

The effect of errors in intensities on phase angles determined by the anomalous-dispersion method. By V. AMIRTHALINGAM* and D. F. GRANT, *Viriama Jones Laboratory, University College, Cardiff, Wales*

(Received 18 December 1962 and in revised form 1 March 1963)

The anomalous-dispersion method for the determination of phases requires the observation of the absolute values of intensities of the (hkl) and $(\bar{h}\bar{k}\bar{l})$ reflexions. These intensities may be in error because of systematic errors introduced by incorrect scaling or incorrect absorption corrections and because of random errors inherent in the method of observation. Ramachandran & Raman (1956) have shown that if the anomalous dispersion is due to a pair of centrosymmetrically related anomalous scatterers (e.g. a pair of heavy atoms in the space group $P2_1$), then the intensity corrected for anomalous scattering (on the absolute scale) is given by

$$F^2 = I = \frac{1}{2}(I_1 + I_2) - (\Delta B)^2$$

where $I_1 = I(hkl)$, $I_2 = I(\bar{h}\bar{k}\bar{l})$, and $\Delta B = (F_{a.s.}/f_{a.s.})\Delta f''$ is the contribution of the anomalous scattering to the imaginary part of the structure factor.

The real and imaginary parts of the structure factors are then given by

$$F_A^2 = \frac{1}{2}(I_1 + I_2) - (\Delta B)^2 - \frac{(I_1 - I_2)^2}{16(\Delta B)^2}$$

and

$$F_B = \frac{(I_1 - I_2)}{4\Delta B}.$$

(The ambiguity of phase is, in practice, resolved by choosing the phase nearest to that of the anomalous scatterer.)

Thus systematic and random errors in I_1 and I_2 will produce errors in the phase angle determined.

Systematic errors

If I'_1 and I'_2 are the observed intensities, then

$$F_B = \frac{k(I'_1 - I'_2)}{4\Delta B}$$

and

$$F^2 = \frac{1}{2}k(I'_1 + I'_2) - (\Delta B)^2$$

where k is a factor necessary to bring the observed intensities to absolute values. Now

$$\sin \alpha = \frac{F_B}{F}$$

and

$$\begin{aligned} \cos \alpha \frac{d\alpha}{dk} &= \frac{1}{F} \frac{dF_B}{dk} - \frac{F_B}{F^2} \frac{dF}{dk} \\ &= \frac{1}{F} \frac{F_B}{k} - \frac{F_B}{F^2} \frac{\frac{1}{2}(I'_1 + I'_2)}{2F} \\ \frac{d\alpha}{dk} &= \frac{\tan \alpha}{k} - \frac{\tan \alpha}{2F^2} \frac{(I'_1 + I'_2)}{2} \\ &= \frac{\tan \alpha}{k} \left\{ 1 - \frac{F^2 + (\Delta B)^2}{2F^2} \right\} \end{aligned}$$

* Colombo Plan Fellow, on deputation from A.E.E.T., Bombay.

or

$$d\alpha = \frac{\tan \alpha}{2} \left\{ 1 - \left(\frac{\Delta B}{F} \right)^2 \right\} \frac{dk}{k}.$$

(The second term of $\{(1 - (\Delta B/F)^2)\}$ may usually be neglected.)

Table 1. $d\alpha$ for values of α and dk/k
($\Delta B/F = 0.2$)

α	dk/k			
	0.10	0.20	0.30	0.40
10°	0.5°	1.0°	1.6°	2.1°
20	1.1	2.2	3.2	4.3
30	1.7	3.4	5.1	6.8
40	2.5	5.0	7.5	10.0
50	3.6	7.1	10.6	14.2
60	5.2	10.4	15.5	20.7
70	8.2	16.4	24.6	32.8

The errors ($d\alpha$) in the phase angle are shown in Table 1 for various values of α and the fractional error (dk/k) in the factor k ; the value of $\Delta B/F$ is here taken as 0.2. If dk/k is due to incorrect scaling then it will be a constant for all reflexions, but if it is due to an incorrect absorption correction then it will depend on the directions of the incident and reflected beams. The table shows that even for moderately large values of dk/k the error in the phase angle is small, except when α approaches 90°.

Random errors

The variance of F_A will be given by

$$\sigma^2(F_A) = \left(\frac{\partial F_A}{\partial I_1} \right)^2 \sigma^2(I_1) + \left(\frac{\partial F_A}{\partial I_2} \right)^2 \sigma^2(I_2)$$

where $\sigma^2(I_1)$ and $\sigma^2(I_2)$ are the variances of I_1 and I_2 . Thus

$$\begin{aligned} \sigma^2(F_A) &= \left\{ \left[\frac{1}{2} - \frac{2(I_1 - I_2)}{16(\Delta B)^2} \right] \frac{1}{2F_A} \right\}^2 \sigma^2(I_1) \\ &\quad + \left\{ \left[\frac{1}{2} + \frac{2(I_1 - I_2)}{16(\Delta B)^2} \right] \frac{1}{2F_A} \right\}^2 \sigma^2(I_2) \end{aligned}$$

and similarly

$$\sigma^2(F_B) = \frac{1}{16(\Delta B)^2} (\sigma^2(I_1) + \sigma^2(I_2)).$$

In the case considered I_1 and I_2 are of nearly the same magnitude and it may be assumed that $\sigma(I_1) = \sigma(I_2) = \sigma(I)$; this is especially so for anomalous scattering when special precautions are usually taken in the intensity measurement (e.g. recording I_1 and I_2 close together on the film).

$$\sigma^2(F_A) = \left[\frac{1}{2} + \frac{(I_1 - I_2)^2}{32(\Delta B)^4} \right] \frac{\sigma^2(I)}{4F_A^2}$$

and

$$\sigma^2(F_B) = \frac{\sigma^2(I)}{8(\Delta B)^2}.$$

Now

$$\sigma^2(\tan \alpha) = \left(\frac{1}{F_A}\right)^2 \sigma^2(F_B) + \left(\frac{F_B}{F_A^2}\right)^2 \sigma^2(F_A)$$

$$= \left\{ \frac{1}{F_A^2} \frac{1}{8(\Delta B)^2} + \frac{F_B^2}{F_A^4} \left[\frac{1}{2} + \frac{(I_1 - I_2)^2}{32(\Delta B)^4} \right] \frac{1}{4F_A^2} \right\} \sigma^2(I)$$

or

$$\sigma(\tan \alpha) = \frac{1}{F \cos \alpha} \left\{ \frac{1}{8(\Delta B)^2} + \frac{F_B^2}{4F_A^4} \left[\frac{1}{2} + \frac{F_B^2}{2(\Delta B)^2} \right] \right\}^{\frac{1}{2}} \sigma(I)$$

$$= \frac{1}{F \cos \alpha} \left\{ \frac{1}{8(\Delta B)^2} + \frac{\tan^2 \alpha}{8F^2 \cos^2 \alpha} + \frac{\tan^4 \alpha}{8(\Delta B)^2} \right\}^{\frac{1}{2}} \sigma(I).$$

Now

$$\sigma(\alpha) = \frac{1}{\sec^2 \alpha} \sigma(\tan \alpha)$$

$$\sigma(\alpha) = \frac{\cos \alpha}{F} \left\{ \frac{1}{8(\Delta B)^2} + \frac{\tan^2 \alpha}{8F^2 \cos \alpha} + \frac{\tan^4 \alpha}{8(\Delta B)^2} \right\}^{\frac{1}{2}} \sigma(I).$$

If $\varepsilon = \sigma(F)/F$ is the fractional error in F then

$$\sigma(\alpha) = \cos \alpha \left\{ \left(\frac{F}{\Delta B}\right)^2 (1 + \tan^4 \alpha) + \frac{\tan^2 \alpha}{\cos^2 \alpha} \right\}^{\frac{1}{2}} \varepsilon.$$

The variation of $\sigma(\alpha)$ with α is shown in Fig. 1; the error in α is reasonably constant up to a phase angle of about 55° , but increases rapidly as α approaches 90° . The value of $\sigma(\alpha)$ for the 'constant' portion will depend on ε and the ratio $F/\Delta B$; Table 2 shows the value of $\sigma(\alpha)$ for this portion for values of ε and the ratio $F/\Delta B$.

Table 2. $\sigma(\alpha)$ for values of ε and $F/\Delta B$

$F/\Delta B$	ε				
	0.01	0.02	0.03	0.04	0.05
2	1.1°	2.3°	3.4°	4.6°	5.7°
5	2.9	5.7	8.6	11.5	14.3
10	5.7	11.5	17.2	22.9	27.6
20	11.5	22.9	34.4	45.8	57.3

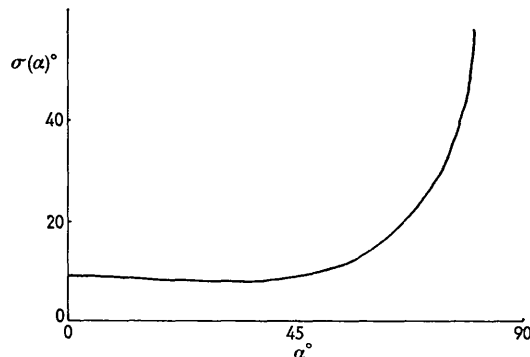


Fig. 1. A graph of $\sigma(\alpha)$ against α for $F/\Delta B=5$ and $\varepsilon=0.03$.

Reference

- RAMACHANDRAN, G. N. & RAMAN, S. (1956). *Curr. Sci.* **25**, 348.

Acta Cryst. (1963). **16**, 852

Unit cell and space group of 4-aminopyridine.* By GEORGE M. BROWN† and HAROLD J. ZABSKY,‡
Department of Chemistry, University of Maryland, College Park, Maryland, U.S.A.

(Received 11 February 1963)

A sample of 4-aminopyridine was kindly furnished by Dr K. G. Stone of Michigan State University. The melting point was $159-161^\circ\text{C}$; the melting point reported by Heilbron (1953) is 158°C . Small irregular crystals of 4-aminopyridine were grown by evaporation of an aqueous solution at room temperature.

Weissenberg and precession photographs (Cu $K\alpha$ radiation) were taken of a single crystal mounted along the c axis of the orthorhombic system found to describe the crystal. Since the only systematic absences noted were the $h00$ reflections for odd h , the $0k0$ reflections for odd k ,

and the $00l$ reflections for odd l , the space group appears uniquely determined as $P2_12_12_1$.

The cell dimensions derived from measurements of the film are: $a=5.57$, $b=7.32$, $c=12.1$ Å, all $\pm 1\%$. The density calculated for $Z=4$ is 1.27 g.cm $^{-3}$; the density observed, by the flotation method, is 1.25 g.cm $^{-3}$.

No crystal specimens were obtained which yielded films suitable for intensity estimation. Diffraction spots were characteristically elongated and drawn out into streaks, evidencing some disorder in growth of the crystals. The structure analysis originally planned was not undertaken.

Reference

- HEILBRON, I. & BUNBURY, H. M. (1953). *Dictionary of Organic Compounds*. Vol. I, p. 133. New York: Oxford University Press.

* This research was supported by the U.S. National Science Foundation.

† Present address: Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

‡ Present address: Chemistry Division, St. Louis University, S. Louis, Missouri.