Parametres cristallins de quelques naphtoquinones 1-4. Par J. Gaultier, *Laboratoire de Minéralogie et de Rayons X. Faculté des Sciences de Bordeaux, France*

Naphtoquinone 1-4

La Naphtoquinone 1-4 cristallise dans le système monoclinique sous forme de prismes jaunes allongés suivant la direction [100]. Les paramètres de maille ont été déterminés à partir des clichés de De Jong et de Bragg:

$$a = 8{,}27 \pm 0{,}02, \quad b = 7{,}86 \pm 0{,}03, \quad c = 12{,}03 \pm 0{,}03 \text{ Å};$$
$$\beta = 80° \pm 30'.$$

Densité calculée: 1,37 g.cm.$^{-3}$.
Nombre de molécules par maille: 4.
Groupe spatial: $P2_1/c$.

Bromo 2-naphtoquinone 1-4

La bromo 2-Naphtoquinone 1-4 cristallise dans le système monoclinique sous forme de plaquettes jaunes allongées suivant la direction [010].
Les paramètres de maille sont les suivants:

$$a = 13{,}88 \pm 0{,}03, \quad b = 3{,}98 \pm 0{,}02, \quad c = 15{,}74 \pm 0{,}03 \text{ Å};$$
$$\beta = 104° \pm 1°.$$

Densité calculée: 1,87 g.cm.$^{-3}$.
Nombre de molécules par maille: 4.
Groupe spatial: $P2_1/c$.

Chloro 2-naphtoquinone 1-4

Ce composé donne difficilement des cristaux propres à l'examen aux rayons X; il se présente sous forme de plaquettes brunâtres allongées suivant la direction [010]. Paramètres de la maille orthorhombique:

$$a = 23{,}84 \pm 0{,}04, \quad b = 3{,}88 \pm 0{,}02, \quad c = 9{,}12 \pm 0{,}02 \text{ Å}.$$

Densité calculée: 1,52 g.cm.$^{-3}$.
Nombre de molécules par maille: 4.
Groupe spatial: $P2_12_12_1$ ou $P2_122_1$.

A correction to photometrically measured intensities to allow for α_1, α_2 splitting. By A. I. M. Rae, *Department of Physics* and W. W. Barker, *Department of Chemistry, University of Western Australia, Nedlands, Western Australia*

When a set of X-ray intensities is measured using a non-integrating camera, the shape of the spots is observed to vary over the film. Four factors may be involved: irregular crystal shape, disorder in the crystal, imperfectly focused X-rays, and increasing separation of the α_1, α_2 doublets. If a micro-photometer is used to measure the intensities, allowance must be made for this change of shape by integrating the area under the photometer trace of each reflection. Brentano (1945) and Buerger (1960) suggest dividing each peak into a number of narrow strips, but these methods are tedious because a large number of measurements are required for each reflection, and are inaccurate when the breadth of the peaks is small. The authors' experience of a number of compounds shows that, in this latter case, the shape of a resolved peak is very frequently triangular to a close approximation. In this paper, it is assumed that a resolved reflection can be represented by a triangle and that doublet separation is the only factor contributing to the variations in line width. The individual α_1 and α_2 traces of a reflection will then be triangles of equal base and the base size will be constant for all reflections. A correction function $C(\theta)$ is derived by which the maximum height of the trace obtained from a reflection of Bragg angle θ should be multiplied to give a measure proportional to the intensity of the reflection.

There are three cases to be considered:

(1) at fairly low Bragg angle where the α_1, α_2 doublets are unresolved;

(2) where resolution occurs but is not complete;

(3) where the doublets are completely resolved.

Case 1

Fig. 1(a) shows the result of combining two triangular peaks of equal base and of heights in the ratio of 1·82:1 (corresponding to the ratio of the peak intensities of Cu $K\alpha_1$ and $K\alpha_2$ radiations respectively) whose centres are separated by a distance $\varDelta < b$ where b is half the base of either triangle and $\varDelta$ is the angular separation of the α_1 and α_2 peaks. It is seen that the position of maximum occurs at the point P. The maximum height H is given by

$$H = h_1 + h_2 - h_2\varDelta/b, \tag{1}$$

where h_1 and h_2 are the heights of the α_1 and α_2 peaks respectively. Now the total area of both triangles is given by

$$A = b(h_1 + h_2). \tag{2}$$

Thus combining (1) and (2), with $r = h_1/h_2$,

$$A = bH\{1 + 1/[(1 + r)b/\varDelta - 1]\}. \tag{3}$$

Now, from the Bragg equation, $\lambda = 2d \sin \theta$,

$$\varDelta = (2\varDelta\lambda/\lambda) \tan \theta, \text{ for } \varDelta \text{ small}, \tag{4}$$

$\varDelta\lambda$ = difference in wavelength between α_1 and α_2 radiations.

The factor 2 appears because the angular movement

of the reflected beam is twice that of the reflecting plane. Thus, substituting in (3)

$$A = bH\{1 + 1/[(1+r)(b\lambda/2\Delta\lambda)\cot\theta - 1]\} \,. \qquad (5)$$

Case 2

In Fig. 1(b) is shown the case where $b < \Delta < 2b$. Here there are two maxima at positions B_1 and B_2 and of heights h_1 and h_2. As $A = b(h_1 + h_2)$, the sum of the maxima is proportional to the intensity, as is the α_1 maximum when multiplied by $(1 + 1/r)$. The latter is more dependable as, especially near $\Delta = b$, h_2 is difficult to measure reliably.
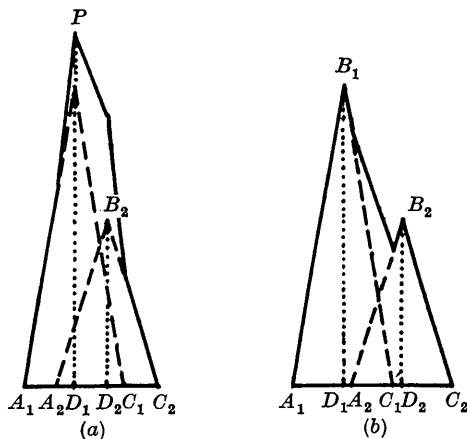
Figs. 1(a) and 1(b). The traces obtained from two triangular peaks, unresolved in 1(a) and incompletely resolved in 1(b). In Fig. 1(a), $PD_1 = H$ and in both 1(a) and 1(b), $A_1D_1 = A_2D_2 = b$, $D_1D_2 = \Delta$, $B_1D_1 = h_1$ and $B_2D_2 = h_2$.
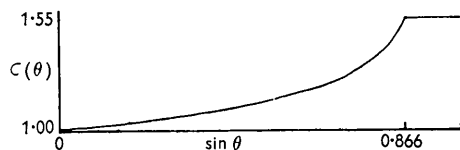

Fig. 2. $C(\theta)$ against $\sin\theta$ with $\theta_0 = 60°$. The discontinuity at $\theta = 60°$ ($\sin\theta = 0.866$) is clearly shown.

Clearly Case 3 will lead to results identical with those in Case 2.

Thus if H is the maximum height of the photometer trace of a reflection at any Bragg angle, θ, then A, and therefore the intensity, will be proportional to $H.C(\theta)$ where

$$C(\theta) = \begin{cases} \{1 + 1/[(1+r)(b\lambda/2\Delta\lambda)\cot\theta - 1]\}, & \theta \le \theta_0 \\ (1 + 1/r), & \theta \ge \theta_0 \end{cases}$$

where θ_0 is that angle at which $\Delta = b$

i.e. $\tan\theta_0 = b\lambda/2\Delta\lambda$ from (4).

Fig. 2 shows a plot of $C(\theta)$ against $\sin\theta$ for $\theta_0 = 60°$, $\lambda = 1.5418$ Å, $\lambda = 0.00382$ Å, $r = 1.81$ and, therefore, $b = 0.00858$ radians. It is seen that considerable errors would arise, particularly near $\theta = \theta_0$, if the intensity were simply taken as proportional to H. In fact, even at $\theta = 20°$ ($\sin\theta = 0.342$), the error involved is about 8%.

Evaluation of b

It can be shown that, in Case 1, the breadth of the trace at half height, σ, is given by

$$\sigma = b + K\tan\theta, \quad \text{for} \quad \theta \le \tan^{-1}[\{(1+r)/(1+2r)\}\tan\theta_0] \,,$$

where $K = 2\Delta\lambda/\lambda(1+r)$.

Thus b should be found by measuring the breadths at half height of a number of low-angle traces, plotting against $\tan\theta$ and extrapolating to $\tan\theta = 0$. In practice, however, $K\tan\theta \ll b$ for $\theta \lesssim \theta_0/3$; thus the arithmetic mean of the breadths of a number of low-angle lines will give quite a good value for b. It should be noted that b must be expressed in radians.

Table 1. *Comparison of $H.C(\theta)$ with A,*
the area of the trace measured by the method of Brentano

hk	$\sin\theta$	$C(\theta)$	H	$H.C(\theta)$	A	$A/H.C(\theta)$
040	0.168	1.09	201	219	613	2.80
060	0.253	1.11	243	269	687	2.55
280	0.413	1.27	208	264	685	2.59
510	0.598	1.53	246	376	1,003	2.67
3,15,0	0.726	1.55	207	321	828	2.58
840	0.970	1.55	119	184	476	2.59

The method has been successfully applied to both single-crystal and powder X-ray data. The shape of the photometer trace at various values of θ agrees well with that obtained from combining two triangles in the manner described above. Measurements have been made of the intensities of the $hk0$ reflections of sulphanilic acid using Cu $K\alpha$ radiation. θ_0 was found to be 38° and Table 1 compares, for several typical reflections, $H.C(\theta)$ with A, the area of the trace measured by subdividing it into strips as described by Brentano (1945) and Buerger (1960). It is seen that the ratio $A/H.C(\theta)$ is constant within a range of about 10%. This is considered satisfactory as the traces were narrow (about 2 or 3 mm.) and thus could not be subdivided accurately.

References

BRENTANO, J. C. M. (1945). *J. Opt. Soc. Amer.* **35**, 382.
BUERGER, M. J. (1960). *Crystal Structure Analysis.* New York: Wiely.