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Determination des mailles et groupes spatiaux de quelques derives anthracèniques.

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Ethyl 9-cyano 10-anthracène $C_{17}H_{13}N$

Le composé se présente sous forme de fines plaquettes jaunes de 0,2 mm. d'épaisseur très propres à l'examen aux rayons X.

Les paramètres de maille déterminés à l'aide de clichés de De Jong et de Bragg sont les suivants:

$$a = 16{,}43,\ b = 8{,}50,\ c = 8{,}70\ \text{Å};\ \beta = 91^\circ\ 30'.$$

Ce cristal appartient au système monclinique, la maille contient 4 molécules et la densité calculée est: $d = 1{,}26$ g.cm.$^{-3}$. Le groupe spatial est $P2_1/c$.

Cyano 9-dihydro 9-10 anthracène $C_{15}H_{11}N$

Le cyano 9-dihydro 9-10 anthracène qui cristallise sous forme de très belles aiguilles incolores de 0,3 mm. de diamètre a pour paramètres de maille:

$$a = 15{,}15,\ b = 21{,}90,\ c = 6{,}77\ \text{Å}\ .$$

Ce cristal de symétrie orthorhombique appartient au groupe spatial *Pbca*. Le nombre de molécules par maille est $z = 8$ et la densité calculée est: $d = 1{,}20$ g.cm.$^{-3}$.

Ethoxy 9-anthracène $C_{16}H_{14}O$

Les cristaux d'ethoxy 9-anthracène d'apparence incolore appartiennent au système orthorhombique. Ils ont pour paramètre de maille a, b, c tels que:

$$a = 13{,}69,\ b = 9{,}48,\ c = 8{,}66\ \text{Å}\ .$$

Le groupe spatial est *Pbcm*. La maille contient 4 molécules et la densité est calculée égale à $d = 1{,}30$ g.cm.$^{-3}$.

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The sensitivity of the correction for extinction in crystals using polarized X-rays and neutrons.

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1. Introduction

Chandrasekhar (1956, 1960) has given a method of correcting X-ray structure factors for extinction in crystals. The method has since been extended (Chandrasekhar & Weiss, 1957) to cover the extinction correction of neutron magnetic structure factors.

For the former case Chandrasekhar (1960) states that the method is 'more powerful the greater the value of θ'. For the latter case no attempt is made to suggest which reflections would be the most sensitive.

In view of the great interest in determining extinction effects, it seems to be worth while to consider the question of sensitivity more carefully.

The notation used here is that used by Chandrasekhar (1960) and Chandrasekhar & Weiss (1957).

2. Calculation of the sensitivity

In the case of X-ray diffraction the amount of extinction can be determined from the measured values of the ratio

$$z = \varrho'_\varphi / \varrho'_\perp\ , \tag{1}$$

where $\varrho'_\perp$ is the integrated intensity of an X-ray reflection when the incident beam is polarized perpendicular to the plane of incidence, ϱ'_φ is the integrated intensity of the same reflection when the incident beam is polarized at an angle φ with respect to the plane of incidence. The natural criterion for the sensitivity of this method is $\partial z/\partial\beta$, i.e. the relative change in z produced by a change in the quantity β, which contains the extinction coefficient. This derivative, which can easily be formed from equation (9) of Chandrasekhar (1960), is

$$\frac{\partial z}{\partial \beta} = \frac{\alpha |F|^2 \cos^2 \varphi}{(\alpha - |F|^2\beta)^2} [\cos^2 2\theta - \cos^4 2\theta]\ . \tag{2a}$$

We have to consider how this derivative depends on θ. This dependence does not lie in the last factor of (2*a*) alone, since α and β are also functions of θ. α is the same for both primary and secondary extinction:

$$\alpha = \left(\frac{Ne^2}{mc^2}\right)^2 \lambda^3 \frac{\int \exp\left[-\mu r\right] dV}{\sin 2\theta} \tag{3}$$

β is different for the two kinds of extinction:

$$\beta_{\text{prim.}} = \left(\frac{Ne^2}{mc^2}\right)^4 \frac{\lambda^5 t_0^2}{3} \frac{\int \exp\left[-\mu r\right] dV}{\gamma_0^2 \sin 2\theta}\ , \tag{4}$$

$$\beta_{\text{sec.}} = \left(\frac{Ne^2}{mc^2}\right)^4 g \lambda^6 \frac{\int r \exp\left[-\mu r\right] dV}{\sin^2 2\theta}\ . \tag{5}$$

In equations (3), (4) and (5) not only the trigonometric functions but also the integrals and γ_0^2 depend on θ. The exact dependence of the latter two can be given if we know the form and dimensions of the crystal and the value of the absorption coefficient μ.

In the case of neutron diffraction the sensitivity of the method may be given by

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$$\frac{\partial y}{\partial \beta}=\frac{|F_N\mp F_P|^2}{\alpha-\beta|F_N\pm F_P|^2}\left[\frac{\alpha-\beta|F_N\mp F_P|^2}{\alpha-\beta|F_N\pm F_P|^2}-\frac{|F_N\mp F_P|^2}{|F_N\pm F_P|^2}\right], \quad (6a)$$

where y is the ratio of the two integrated intensities taken with the two opposite directions of polarization (Chandrasekhar & Weiss, 1957). The upper signs should be taken if F_N and F_P have the same sign and the lower signs in the opposite case. The explicit dependence on θ lies here in α and β.*

3. Discussion

We may see from equations (2a) and (6a), respectively, that the sensitivity depends not only on the values of the structure factors but also explicitly on θ.

In the X-ray case, equation (2a), this explicit dependence is not monotonic but has minima equal to zero at $\theta=0°$, 45° and 90°. The statement of Chandrasekhar quoted in our Introduction is thus incomplete. This may be understood in simple physical terms. Only such quantities can be determined from z which have effect on its value. At $\theta=0°$ and 90° the intensity is obviously independent of the direction of polarization, and consequently z is equal to 1, independently of the value of β. At $\theta=45°$, $z=\sin^2\varphi$, again entirely independently of the value of β. Thus β cannot be determined from z in these cases. Positions and values of the maxima depend upon the factors mentioned in Section 2 and can be computed from equation (2a).

In many practical cases, the crystal is in the form of a cylinder or of a pillar with approximately square cross section. If, in addition, the absorption is small it is easy to calculate these maxima. The integral and γ_0^2 in equation (4) vary only slightly with θ in this case and can be regarded as constants. With primary extinction alone, the first factor of $\partial z/\partial\beta$ depends then on θ as $\sin 2\theta$:

$$(\partial z/\partial\beta)=\text{const.}\,|F|^2\cos^2\varphi.\sin 2\theta\,[\cos^2 2\theta-\cos^4 2\theta]\,. \quad (2b)$$

It is easy to show that the maxima are at $\theta=25{\cdot}4°$ and $64{\cdot}6°$. With secondary extinction alone the θ dependence is a little more complicated, but if, besides the assumptions made above, we make use of the assumption inherent in the theory of Chandrasekhar that the extinction is weak, $\partial z/\partial\beta$ has virtually the same form as in the case of primary extinction.

The effect of the structure factor on the sensitivity is simple in the X-ray case. In consequence of the smallness of β, the sensitivity is approximately proportional to $|F|^2$.

The sensitivity in the neutron case, given by equation (6a), has similarly an explicit dependence on θ, due to its dependence on α and β. $\partial y/\partial\beta$ takes a very simple form as regards the explicit θ dependence if we use the same approximation as in the X-ray case:

$$\frac{\partial y}{\partial\beta}=\text{const.}\,|F_N\mp F_P|^2\left[1-\frac{|F_N\mp F_P|^2}{|F_N\pm F_P|^2}\right]\cdot\sin 2\theta\,. \quad (6b)$$

* In this case e^2/mc^2 should be replaced by 1 in the formulas.

This has minima equal to zero at $\theta=0°$ and 90°. The reason for this is the same as in the X-ray case. At $\theta=45°$ there is now maximum sensitivity, in contrast to the X-ray case.

The dependence of the sensitivity on the structure factor is, on the other hand, much more complicated than in the X-ray case, both in the general equation (6a) and in the approximate equation (6b). The sensitivity is O in the latter for reflections at which $|F_N\mp F_P|=0$ or $|F_N\mp F_P|=|F_N\pm F_P|$ and is very small if these equalities nearly hold. (The use of the signs as stated above should be kept in mind here.) These are cases in which $y=0$ and 1, respectively, independently of the value of β.

We have thus seen that this method of correcting for extinction is restricted to a part of the measurable reflections. Our formulas (2a) or (2b), and (6a) or (6b), respectively, should be used to determine the accuracy of the extinction determination, the value of which may otherwise be very doubtful. On ground of these formulas the reflections which are suitable for the determination of the extinction with prescribed accuracy can be chosen and the necessary accuracy of intensity measurements can be determined.

The limitation of the method is not severe if we may suppose that only secondary extinction occurs in our measurements. It is then sufficient to determine $\beta=\beta_{\text{sec.}}$ from the reflections (in principle from one of these) at which the sensitivity is high enough and compute $\beta_{\text{sec.}}$ by equation (5) for the other reflections at which it cannot be measured with sufficient accuracy.

The limitation is more restrictive if this latter simplification is not justified. In this case $\beta=\beta_{\text{prim.}}+\beta_{\text{sec.}}$. It is thus necessary to know both t_0^2, equation (4), and g, equation (5), to compute β for reflections at which it cannot be measured with sufficient accuracy. Measurement of β at two reflections for which $\sin 2\theta$ is different would be sufficient in principle for this purpose. It is easy to show, however, that the decomposition of β into $\beta_{\text{prim.}}$ and $\beta_{\text{sec.}}$, i.e. the determination of t_0^2 and g can be made the less accurately the smaller the difference between the $\sin 2\theta$ values of these two reflections. Although this method accounts for both primary and secondary extinction simultaneously at the reflections at which it is used directly, the transference of this situation to reflections for which the extinction can be determined only indirectly has thus severe restrictions.

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