nous attendons l'achèvement d'une étude de spectrométrie infra-rouge entreprise par A. Novak sur ces 3 formes.

Références

ALLÉAUME, M. & DECAP, J. (1965). *Acta Cryst.* **18**, 731.
CLASTRE, J., ALLÉAUME, M. & BOUZON, C. (1964). *Bull. Soc. Franç. Minér. Crist.* **87**, 434.
CRUICKSHANK *et al.* (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* Paper 6, 32.
O'CONNOR, B. H. & MASLEN, E. N. (1965). *Acta Cryst.* **18**, 363.
PENFOLD, B. R. & WHITE, J. C. B. (1959). *Acta Cryst.* **12**, 130.
WATANABE, A. (1941). *Naturwissenschaften*, **29**, 116.
WATANABE, A. (1942). *J. Pharm. Soc. Japan*, **62**, 503.

Acta Cryst. (1965). **19**, 938

Collimation Corrections in Small Angle X-ray Scattering*

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An improved technique is developed for correcting experimental small angle X-ray scattering data for the effects of the height of the collimating slits when the weighting function for the intensity distribution along the slit height can be approximated by a Gaussian. Although the new correction method is no more difficult to use than an earlier technique [Schmidt & Hight, *Acta Cryst.* **13**, 480 (1960)], the corrected intensity values are considerably more accurate when there is negligible error in the input data. The new method also has the advantage of being less sensitive to errors in the input data.

Introduction

Experimental measurements of the angular distribution of the intensity of small angle X-ray scattering, instead of giving the scattering at a single angle, ordinarily represent the average intensity over a range of angles around the nominal scattering angle. In order to obtain sufficient scattered intensity, this range of angles often must be made so large that the scattering pattern is appreciably distorted. The experimental scattering data must then be corrected for this effect.

Most collimating systems employ slits with a length much greater than their width. Since the slit width can usually be assumed small enough that it has a negligible effect on the scattering pattern, only the effects of slit height will be considered here.

For slits of negligible width, the experimentally measured scattering intensity $F(h)$ is related to the perfect-collimation scattering $I(h)$ by the equation (Guinier, Fournet, Walker & Yudowitch, 1955)

$$F(h)=\int_0^\infty d\varphi W(\varphi)I\left(\sqrt{h^2+\varphi^2}\right) \qquad (1)$$

where h is the scattering angle and $W(\varphi)$ is a weighting function which depends on the collimating system. The weighting function $W(\varphi)$ will be assumed to be known from calculations or experimental measurements. It will be normalized so that

$$\int_0^\infty W(\varphi)d\varphi=1\ .$$

In order that the integration in (1) need extend only over positive values of φ, $W(\varphi)$ is assumed to be an even function of φ. With this notation, collimation correction consists in finding $I(h)$ from $F(h)$. The form of $W(\varphi)$ determines the mathematical procedures necessary for this correction.

Often $W(\varphi)$ can be approximated by a Gaussian. Kratky, Porod & Kahovec (1951) showed that for a Gaussian weighting function $W(\varphi)=2p\pi^{-\frac{1}{2}}\exp(-p^2\varphi^2)$,

$$I(h)=-\frac{\exp(p^2h^2)}{p\pi^{\frac{1}{2}}}\int_h^\infty \frac{N'(t)dt}{(t^2-h^2)^{\frac{1}{2}}} \qquad (2)$$

where $N(h)=F(h)\exp(-p^2h^2)$. The constant p is determined by the slit height, with perfect collimation corresponding to the limit of infinite p, and with the weighting function for infinite slit height being obtained by letting $p=0$ in the exponential function and then assigning some convenient value to the factor by which the function is multiplied. Thus, for infinite slit height, $W(\varphi)$ is a constant and no longer satisfies the normalization relation.

To use (2) to find $I(h)$, the experimental data must be differentiated numerically. Because of the need to perform this differentiation, the relative error in $I(h)$ can be greater than the relative error in the experimental data.

A number of methods have been proposed for collimation correction. Kratky, Porod & Skala (1960) discussed some procedures for collimation correction, and Heine & Roppert (1962) and Heine (1963) developed techniques for performing collimation corrections with an automatic digital computer. Methods for ma-

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chine computation of collimation corrections for infinite slit height were recently described by Kent & Brumberger (1964), and by Chu & Tan Creti (1964).

By modifying equation (1), Schmidt & Hight (1960) obtained an expression giving $I(h)$ directly in terms of $F(h)$, instead of $N'(h)$. For several years this technique has been used routinely in correcting experimental small angle X-ray scattering data. Although this method gave satisfactory results in almost all cases, an effect was observed which suggested that further study of the collimation correction problem was advisable. When the scattered intensity did not change by more than a factor of the order of two throughout the angular region for which data were available, the corrected data points often did not lie on a smooth curve but instead would be scattered randomly about an average curve. This effect was observed only for these relatively slowly changing scattering curves. Preliminary tests indicated that it was due to small errors in the experimental data and suggested the advisability of studying the sensitivy of the corrected curve to small random errors in the scattering data. Also, the availability of automatic digital computers made feasible a relatively extensive investigation of the errors introduced by collimation correction methods when there is negligible error in the input data.

This discussion of collimation correction procedures thus considers two effects. First, several collimation correction methods are studied to determine the error introduced by the correction procedure when there is essentially no error in the input data. Also, the correction methods are tested for their sensitivity to random errors in the experimental data. The results of these investigations are used to develop a collimation procedure which is an improvement over the method of Schmidt & Hight.

The collimation correction techniques and the results of the tests are summarized below. A more detailed account is available from the author.

Numerical methods

As Schmidt & Hight (1960) pointed out, the principal advantage of their modified equation is that it can often simplify the calculations. Both the modified equation and equation (2) contain the same information and in principle should give equivalent results. The choice of which equation to use is primarily a matter of convenience. For the present series of numerical calculations, (2) was chosen as a starting point.

For numerical evaluation, (2) can be written

$$I(h)=-\frac{\exp(p^2h^2)}{p\pi^{\frac{1}{2}}}\sum_{i=0}^{\infty}\int_{(j+i)\Delta}^{(j+i+1)\Delta}\frac{dsN'(s)}{\sqrt{s^2-h^2}}. \quad (3)$$

In this expression j is taken to be an integer, with $h=i\Delta$. In (3), a change of the variable of integration gives

$$I(h)=-\frac{\exp[(pj\Delta)^2]}{p\Delta\pi^{\frac{1}{2}}}\sum_{i=0}^{\infty}\int_{j+i}^{j+i+1}\frac{dm}{\sqrt{m^2-j^2}}\frac{d}{dm}[N(m\Delta)]. \quad (4)$$

In each integral of the sum, $N(m/\Delta)$ will be assumed to be approximated by a polynomial such that $d/dm\times[N(m/\Delta)]$ can be written

$$\frac{d}{dm}[N(m\Delta)]=\sum_{k=0}^{5}[a_{k-2}+(m-j-i-1)b_{k-2}+(m-j-i-1)^2c_{k-2}]N_{j+i+k-2} \quad (5)$$

where $N_j=N(j\Delta)$ and a_{k-2}, b_{k-2}, and c_{k-2} are constants determined by the particular conditions chosen to define the polynomial. In certain cases some of these constants can be zero. Let $F_j=F(j\Delta)$. Then (5) can be used to express (4) in the form

$$I(j\Delta)=\sum_{i=0}^{\infty}T_{ij}F_{j+i-2}. \quad (6)$$

In (6) the slit-corrected intensity thus is a sum of terms which are the product of the experimental intensity values F_j and constants T_{ij} which depend only on the collimation system and which are the same for all scattering curves measured under the same collimation conditions. Equation (6), which is similar to but not identical with the final equation of Schmidt & Hight, is in a convenient form for numerical computation.

When linear and quadratic polynomials were used to approximate $N(m\Delta)$ in (4), the results were no better than those obtained with the method of Schmidt & Hight. Therefore, in all other studies $N(m\Delta)$ was approximated by a cubic polynomial. Thus $d/dm[N(m\Delta)]$ was a quadratic function of m, as in (5).

For the interval $j\le m\le j+1$ a cubic polynomial is uniquely determined by requiring the polynomial to equal the experimental values of $N(m\Delta)$ at four points where the function is known from experimental data. Four convenient values for the interval $j\le m\le j+1$ are given by N_{j-k} with $k=-1$, 0, 1, and 2. Alternatively, one could use the four N_{j+k} with $k=0$, 1, 2, and 3 or with $k=-2$, -1, 0, and 1. All three of these cubic polynomials were tested and gave nearly equivalent results. For all three polynomials, the accuracy of collimation correction was very satisfactory, but random errors in $F(h)$ produced large fluctuations in the corrected scattering data.

In order to reduce these effects of random errors, another cubic polynomial approximation for $N(m\Delta)$ in the interval $j\le m\le j+1$ was written in the form

$$N(m\Delta)=A_j+(m-j)B_j+(m-j)^2C_j+(m-j)^3D_j,$$

the constants A_j, B_j, C_j, and D_j being determined by the condition that for each j, the polynomial be a least-squares fit to the six values of N_{j-k} given by $k=-2$, -1, 0, 1, 2, and 3. For a given value of j, the least-squares fit requires that the quantity

$$S_j = \frac{1}{N_j}\left\{\frac{1}{6}\sum_{k=0}^{5}\left[N\left(\frac{j+k-2}{2}\Delta\right) - N_{j+k+2}\right]^2\right\}^{\frac{1}{2}}$$

be a minimum. For the polynomial defined by this condition, the T_{ij} in (6) are given by

$$T_{ij} = U_{i-2,j}[V^1_{ij} + V^2_{ij} + V^3_{ij}] \tag{8}$$

where

$$U_{ij} = (p\Delta)^{-1}\pi^{-\frac{1}{2}} \exp\left[(p\Delta)^2(2ij+j^2)\right]$$
$$V^1_{ij} = \Delta^1 S^1_{i-2,j} - \tfrac{5}{63}\Delta^5 S^1_{i-4,j}$$
$$V^2_{ij} = \Delta^2 S^2_{i-3,j} + \tfrac{5}{14}\Delta^4 S^2_{i-4,j} + \tfrac{5}{126}\Delta^5 S^2_{i-4,j}$$
$$V^3_{ij} = \Delta^3 S^3_{i-3,j} + \tfrac{5}{18}\Delta^5 S^3_{i-4,j} \tag{9}$$

with $S^k_{ij} = 0$ for all k and j when $i \leq 0$, and for $i \geq 1$,

$$S^1_{ij} = \int_{i+j-1}^{i+j} \frac{dm}{\sqrt{m^2-j^2}}$$
$$S^2_{ij} = -\int_{i+j-1}^{i+j} \frac{dm}{\sqrt{m^2-j^2}}\left[m-i-j+\tfrac{1}{2}\right]$$
$$S^3_{ij} = \frac{1}{2}\int_{i+j-1}^{i+j} \frac{dm}{\sqrt{m^2-j^2}}\left[(m-i-j)^2-\tfrac{1}{3}\right] \tag{10}$$

and where for the quantity f_i the nth difference $\Delta^n f_i$ is defined

$$\Delta^n f_i = \sum_{k=0}^{n} \frac{(-1)^n n!}{k!(n-k)!} f_{i+k}. \tag{11}$$

For scattering curves which are changing relatively rapidly, a smaller interval of integration may be necessary to give corrected data with sufficient accuracy. To reduce the number of terms which must be considered in making collimation corrections with a reduced interval of integration, a smaller interval, which will be called Δ, can be used near the lower limit of (3), an interval 2Δ being employed in the rest of the integral. An analogue of (6) has been developed using these two intervals of integration. Further information about the resulting equation, which will be referred to as the 'variable increment equation', is available from the author.

Results

Six test functions were used to compare and evaluate the different collimation correction methods. For the test functions, $I(h)$ could be represented by the relation

$$I(h) = I_n(h,a) = h^n \exp(-a^2h^2),$$

$I_2(h,a)$, $I_4(h,a)$, $I_0(h,a)$, $I_0(h,0)$, $I_{-2}(h,0)$, and $I_{-4}(h,0)$ being employed in the tests. Note that $I_0(h,a)$ is a Guassian, and $I_0(h,0) = 1$. The corresponding $F(h)$ functions $F_n(h,a)$ computed from (1) can be expressed in terms of tabulated functions. A list of the $F_n(h,a)$ and tables of their values are available from the author.

This set of test functions was chosen to provide a convenient way of evaluating the collimation correction methods under conditions similar to those likely to be encountered in experimental small angle X-ray scattering studies.

Tests were made of (6), the variable increment equation, and several equations using other approximations for $N'(s)$. In all calculations, p was set equal to $(225/8)\pi^{\frac{1}{2}}$, in order to simulate the experimental conditions at the University of Missouri. For Δ, values of 0·001, 0·0005, and 0·000125 radian were employed in (6), and in the tests of the variable increment equation, the increments were 0·0005 and 0·001 radian. In the test functions $F_2(h,a)$, $F_4(h,a)$, and $F_0(h,a)$, the constant a was equal to 286, 440, and 50, respectively, with h expressed in radians.

The calculations were made with an IBM 1620 Model I computer. FORTRAN II-D programs were prepared for computing the T_{ij} and for making collimation corrections with (6) and the variable increment equation. At angles less than 20 milliradians, with 100 T_{ij} values used for each angle, the computing time was about 3 seconds at each angle.

The results of the tests are summarized in Table 1.

Table 1. *Maximum percentage error obtained for test functions $F_n(h, a)$ expressed to k significant figures, using equation* (6) *and the variable increment* (*v.i.*) *equation*

Test function	k	Equation	Angular region (milliradians) 3–5	6–9	10–20
F_0 $(h,0)$	8	6	0·005	0·002	0·004
F_0 (h,a)	4	6	0·02	0·02	0·03
F_0 (h,a)	2	6	2	2	3
F_0 (h,a)	2	v.i.	2	2	—
F_2 (h,a)	4	6	3	4	—
F_2 (h,a)	2	6	3	4	—
F_2 (h,a)	4	v.i.	0·3	1	—
F_2 (h,a)	2	v.i.	4	2	—
F_4 (h,a)	4	6	5	—	—
F_4 (h,a)	2	6	4	—	—
F_4 (h,a)	2	v.i.	2	—	—
F_4 (h,a)	4	v.i.	1	—	—
$F_{-2}(h,0)$	4	6	4	0·2	0·04
$F_{-2}(h,0)$	2	6	4	3	3
$F_{-2}(h,0)$	4	v.i.	0·1	0·06	—
$F_{-2}(h,0)$	2	v.i.	5	1	—
$F_{-4}(h,0)$	4	6	200	0·5	0·3
$F_{-4}(h,0)$	2	6	200	2	3
$F_{-4}(h,0)$	4	v.i.	0·3	0·1	—
$F_{-4}(h,0)$	2	v.i.	2	2	—

As all collimation correction equations gave essentially satisfactory results at angles greater than 20 milliradians, this range of angles will not be discussed. No errors are shown for $F_4(h,a)$ for 6–9 milliradians because in this region the function was decreasing too rapidly to give meaningful values of $I(h)$.

The constant test function $I_0(h,0) = F_0(h,0)$ can be considered a test of the error inherent in the numerical approximation used to evaluate $N(m\Delta)$ in (4), since for a constant test function, $F(h)$ is expressed to the same number of significant figures that the computer uses in all steps of the computations, and thus there are essentially no random errors in $F(h)$. Thus, as Table 1 in-

dicates, the error in $I_0(h,0)$ is much lower than for any of the other $I_n(h,a)$. The low errors are due to the very favorable conditions under which the method was tested, and such high accuracy cannot be expected when the input function $F(h)$ has no more than 4 significant figures.

To test the effects of random errors in the input data, the test functions were expressed to four, three, and two significant figures. Random errors were found to cause appreciable scatter of the corrected intensity values only for scattering curves which changed relatively slowly. Apparently this effect is not merely a consequence of the scatter being more easily observed when the intensity is slowly changing, but is also due to the fact that for a slowly changing intensity curve, the corrected intensity is a small difference of a number of larger terms, while for more rapidly changing scattering curves, a greater fraction of the corrected intensity comes from the first few terms of (6) and the variable increment equation.

With most of the polynomial approximations for $N'(s)$, and with the method of Schmidt & Hight, scatter appeared in the corrected intensity when the input data were rounded off to two significant figures. When the data were expressed to more significant figures, no scatter was observed. As can be seen from Fig. 1, use of the least-squares approximation nearly eliminated the scatter in the corrected data for $\Delta = 0{\cdot}001$ radian when $F_0(h,a)$ was expressed to 2 significant figures. This smoothing effect was also found in other scattering curves.

The tests showed that decreasing the increment Δ did not always increase the accuracy of the corrected scattering data. For example, in one case when the variable increment equation was used with increments of 0·0005 and 0·001 radian and with the test function expressed to two significant figures, much more scatter was observed in the corrected results than was found from (6) with the same input and with $\Delta = 0{\cdot}001$ radian.

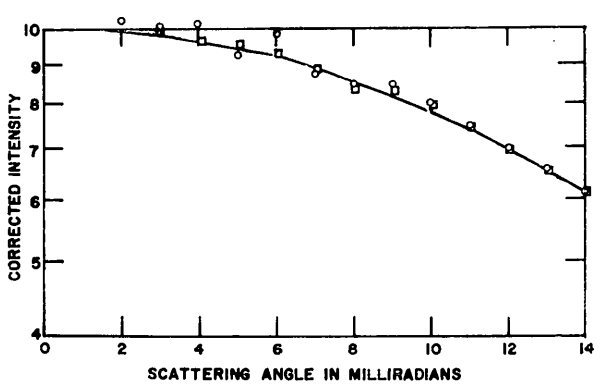

Fig. 1. Collimation corrections for the Gaussian test function pair $I_0(h,a)$ and $F_0(h,a)$. The exact values of $I_0(h,a)$ are shown by the curve, and squares and circles indicate $I_0(h,a)$ values calculated by (6) and by the method of Schmidt & Hight, respectively, with the input function $F_0(h,a)$ expressed to two significant figures in both cases.

Thus, in this situation, decreasing the increment increased the error. This effect is probably a result of the dependence of the corrected curve on the derivative of the input data. For a constant absolute error in the input data, decreasing the increment increases the uncertainty in the derivative. Because of this effect, care must be given to the choice of Δ for a given experimental situation.

As Table 1 indicates, the variable increment equation gives a lower error than (6) only in angular regions where $F(h)$ either has a maximum, like $F_2(h,a)$ and $F_4(h,a)$ in the region from 3 to 5 milliradians, or when $F(h)$ is changing relatively rapidly, like $F_{-4}(h,0)$ at angles between 3 and 5 milliradians. In other cases, the variable increment equation does not give an appreciably smaller error in $I(h)$ than is obtained with (6). Also, as has been mentioned above, a decrease in the increment can increase the probability of random errors in $I(h)$. For these two reasons, routine use of the variable increment equation is not recommended for the inner part of the scattering curve. Instead, the tests suggest that ordinarily (6) should be used for routine collimation corrections, the variable increment equation being applied in the inner part of the scattering curve only when the experimental intensity in this angular region either has maxima or minima or is changing relatively rapidly. In doubtful cases the experimental values of $F(h)$ can be corrected by both equations, and the choice of which equation is best can be made after comparison of values of $I(h)$ obtained by the two equations.

The test functions $F_n(h,a)$ were also used as input data for the collimation correction technique of Schmidt & Hight, in order to compare the results of this method with those from (6) and the variable increment equation. With the method of Schmidt & Hight, the corrected intensity usually was accurate within about 1%, although for rapidly changing functions the error was somewhat greater. Except in this case, however, the errors introduced by the method of Schmidt & Hight are no larger than would be encountered in experimental data, and thus the errors ordinarily are not appreciable.

Because of the higher accuracy of (6) and the variable increment equation and their reduced sensitivity to errors in the input data, these equations, once the T_{ij} are computed, represent an improved collimation correction technique which is no more difficult to use than the method of Schmidt & Hight.

Copies of the IBM 1620 programs for evaluating equation (6) and the variable increment equation are available from the author.

The author would like to express his gratitude to the staff of the University of Missouri Computer Research Center for authorizing the use of the computer and for assistance with the numerical calculations, and to Robert E. Harris for suggesting the use of the least-squares technique and for other helpful discussions.

References

CHU, B. & TAN CRETI, D. M. (1964). *Acta Cryst.* **18**, 1083.
GUINIER, A., FOURNET, G., WALKER, C. B. & YUDOWITCH, K. (1955). *Small Angle Scattering of X-rays.* p. 114, equation 10. New York: Wiley.
HEINE, S. & ROPPERT, J. (1962). *Acta Phys. Austriaca,* **15**, 148.
HEINE, S. (1963). *Acta Phys. Austriaca,* **16**, 144.
KENT, P. & BRUMBERGER, H. (1964). *Acta Physica Austriaca,* **17**, 263.
KRATKY, O., POROD, G. & KAHOVEC, L. (1951). *Z. Elektrochem.* **55**, 53.
KRATKY, O., POROD, G. & SKALA, Z. (1960). *Acta Phys. Austriaca,* **13**, 76 (1960).
SCHMIDT, P. W. & HIGHT, R., JR. (1960). *Acta Cryst.* **13**, 480.

Acta Cryst. (1965). **19**, 942

The Crystal Structure of 2,2′-*p*-Phenylenebis-(5-phenyloxazole) – 'POPOP'*

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The crystal structure of the organic scintillator POPOP, 2,2-*p*-phenylenebis-(5-phenyloxazole), has been determined and refined by three-dimensional least-squares methods. The final R index for 1370 observable reflections is 0·058, and the standard deviations in the positions of the C, N, and O atoms are about 0·003 Å.

The crystals are monoclinic, space group $P2_1/c$, with $a=9{\cdot}230$, $b=5{\cdot}285$, $c=19{\cdot}322$ Å and $\beta=92{\cdot}09°$; there are two centrosymmetric molecules per unit cell. The three benzene and two oxazole rings are each planar, but they are twisted slightly with respect to one another to form a propeller-shaped molecule. The bond distances indicate appreciable conjugation between the rings and localization of charges within the oxazole rings. The intermolecular contacts appear to be normal.

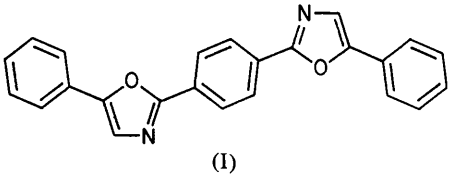
Introduction

POPOP, $C_{24}H_{16}N_2O_2$(I), with the structural names:

(*a*) 2,2′-*p*-phenylenebis-(5-phenyloxazole)

(*b*) 1,4-bis-2-(5-phenyloxazolyl)benzene

is a scintillator, capable of emitting a brief pulse of fluorescent light upon interaction with a high-energy particle or quantum (*e.g.*, Bell & Hayes, 1958).



(I)

An X-ray diffraction study has been completed of the molecular structure of this strong scintillator.

Experimental

Scintillation-grade crystals of POPOP were obtained from Packard Instrument Company. They occur as long, pale yellow needles, with the needle axis parallel to the crystallographic b axis. The crystals are soft and have no pronounced cleavage, and as a result all attempts to obtain a specimen suitable for mounting about any axis other than b were unsuccessful. The crystal used for collecting intensity data was about 0·07 × 0·07 mm in cross section and about 3 mm in length.

The unit-cell dimensions and other crystal data are given in Table 1. Values for a, c, and β were determined from a least-squares treatment based on 34 high-angle ($\sin\theta > 0{\cdot}81$) $h0l$ reflections measured on a Straumanis-type rotation photograph about **b**; the value of b was obtained from a weighted average of 270 measurements made on precession photographs, taken with Mo and Fe radiation, of the $hk2h$ zone and calibrated from the previous values of a, c, and β.

Table 1. *Unit cell parameters of POPOP and their estimated standard deviations*

($\lambda_{Cu\ K\alpha}$ = 1·5418 Å)

$a=$ 9·2300(3) Å	$V=941{\cdot}9(3)$ Å^3
$b=$ 5·2850(8)	$Z=2$
$c=19{\cdot}3220(7)$	$\varrho_c=1{\cdot}285(1)$ g.cm^{-3}
$\beta=92{\cdot}088(2)°$	$\varrho_o=1{\cdot}306(10)$ g.cm^{-3}

In the least-squares treatment of the $h0l$ data, weights on an absolute scale were derived from the distribution of discrepancies between repeated measurements; the resulting goodness of fit was 0·8, suggesting that the

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